

For Reference

NOT TO BE TAKEN FROM THIS ROOM

For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex LIBRIS
UNIVERSITATIS
ALBERTAEENSIS





Digitized by the Internet Archive
in 2020 with funding from
University of Alberta Libraries

<https://archive.org/details/JDean1967>

THE UNIVERSITY OF ALBERTA

THEORETICAL SLOPE METHOD OF

END POINT DETECTION

by

JOHN R. DEAN, B.Sc., M.Sc.



A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE
STUDIES IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

NOVEMBER, 1967

THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES

The undersigned hereby certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled THEORETICAL SLOPE METHOD OF END POINT DETECTION submitted by John R. Dean, B.Sc., M.Sc., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

CONTENTS	Page
ABSTRACT	iv
ACKNOWLEDGEMENTS	vii
LIST OF TABLES	viii
LIST OF FIGURES	x
PRINCIPAL SYMBOLS	xiv

CHAPTER 1

INTRODUCTION

1.01	Amperometric Titrations	3
1.02	Amperometric Indicators	10
1.03	Photometric Indicators	18
1.04	Comparison of Titration Systems Involving Amperometric and Photometric Indicators	21

CHAPTER 2

END POINT DETECTION IN AMPEROMETRIC AND PHOTOMETRIC TITRATIONS WITH UNFAVORABLE EQUILIBRIUM CONSTANTS

2.01	The Extrapolation Method of End Point Detection as Applied to the First End Point	24
2.02	Methods of End Point Detection Involving Calculation	30
2.03	Theoretical Slope Method of End Point Detection	34

2.04	The Correction Factor in the Theoretical Slope Method	40
2.05	Recommended Procedure for the Use of the Theoretical Slope Method	49

CHAPTER 3

STATISTICAL RESULTS

3.01	Statistical Investigation of Factors that Influence the Precision of the Extrapolation method of End point detection	55
3.02	Statistical Investigation of the Effect of the Ratio of the Conditional Equilibrium Constants on the Precision and Accuracy of the Extrapolation Method of End point detection	66
3.03	Summary of Statistical Investigation	77

CHAPTER 4

EXPERIMENTAL RESULTS

4.01	Copper (II) as an Amperometric Indicator Ion for the Determination of Thorium	79
4.02	Cadmium as an Amperometric Indicator for the Determination of Gadolinium, Samarium, Neodymium and Zinc, Using EDTA as the Titrant.	99
4.03	Copper as a Photometric Indicator for the Determination of Calcium	119

CHAPTER 5

CONCLUSION

I3I

BIBLIOGRAPHY

I35

APPENDIX

I39

ABSTRACT

When reactions go to completion the end point in an amperometric or photometric titration can be precisely and accurately located by the so called tangent or extrapolation method. The method involves extending the two linear portions of the titration curve until they intersect.

In this thesis, a statistical investigation of the extrapolation method was carried out in order to obtain an indication of the limits of its precision and accuracy. Evidence was obtained to indicate that the acute angle between the extrapolated lines has an effect on the end point precision. The best precision is obtained when the angle approaches 90° and deteriorates seriously when less than 30° . Additional evidence was obtained to indicate that the extent of extrapolation also effects the end point precision. The best values are obtained when little or no extrapolation is required, i.e., when the lines are almost entirely established by points ($\geq 70\%$).

Amperometric and photometric titrations may be carried out in some cases by addition of a metal ion species called a metal ion indicator. The ratio of the conditional equilibrium constant of the metal-to-be-determined -titrant complex to the conditional equilibrium constant of the metal-ion-indicator-titrant

complex affects the precision and accuracy of the extrapolation method of end point detection. The extrapolation procedure was applied to five computer calculated titration curves. The best precision is obtained when the ratio of conditional equilibrium constants is about 10^3 or greater. For lower ratios the precision deteriorates rapidly. A conditional equilibrium constant ratio of at least 10^2 gives the best accuracy. The accuracy deteriorates rapidly for lower ratios.

Thorium was titrated amperometrically using copper (II) as the amperometric indicator and EDTA as the titrant. A relative precision of 0.8% was obtained with 133 μ g. of thorium by applying the extrapolation procedure. The ratio of conditional equilibrium constants for this system was calculated to be $10^{3.4}$.

A rapid and precise method, called the theoretical slope method, is proposed for titrations involving a metal ion indicator in which the extrapolation method is unsuitable because the ratio of conditional equilibrium constants is too low. The method, in most cases, requires a prior determination of the ratio of conditional constants. Statistical data shows that the theoretical slope method gives better accuracy and in some cases better precision is also indicated.

When the proposed theoretical slope method was used to detect the end point in the titration of 5×10^{-5} moles of

gadolinium, samarium, neodymium or zinc using cadmium as the amperometric indicator and EDTA as the titrant, an accuracy and relative precision of 1 to 3% was obtained. Each of these systems has a ratio of conditional equilibrium constants of less than 10.

Because of its speed, the theoretical slope method is also recommended as a substitute for the extrapolation method in systems where the ratio of conditional equilibrium constants is greater than 10^2 .

ACKNOWLEDGEMENTS

I wish to acknowledge the guidance and encouragement of my research advisor, Professor W. E. Harris. It was a privilege and a pleasure to work with him. Any polish in the presentation of this thesis is primarily the result of his advice.

I wish also to especially acknowledge the patience, love and understanding displayed by my wife, Eleanor, during these years. The sometimes intangible and always appreciated encouragement provided by my parents during all my university years are too numerous to mention but will always be remembered and sincerely appreciated.

The last, but by no means the least acknowledgment I wish to give to Mrs. Wendy Johnson who did such an excellent job in the typing of this manuscript. Her personal consideration of my thesis is a difficult quality to find in a typist.

LIST OF TABLES

Table	Title	Page
1.01	Electrochemical Behaviors of Reactants Corresponding to Various Types of Amperometric Titration Curves.	9
2.01	The Conductometric Titration of KCl with NaClO ₄ .	29
2.02	Computer Calculated Results for the Reaction of Titrant with, M ⁺ⁿ and Ind ^{+x} in a mole ratio of 1.0 to 0.4 and with a Value of (K' _{MT} ⁺ⁿ /K' _{IndT} ^{+x}) of 100.	44
3.01	Results of Statistical Investigation of the Effect of the Angle Between the Extrapolated Lines on the Precision with which the Intersection can be Read.	60
3.02	Results of the Statistical Investigation of the Effect of ϕ on the Precision of the Extra- polation Procedure when the Acute Angle Between the Lines is 76°.	63
3.03	Results of End Point Detection by the Two Extrapolation Procedures.	68
3.04	Results of End Point Detection by the Theoretical Slope Method.	70
4.01	Results of Titrating Various Amounts of Thorium with 2×10^{-2} M to 4×10^{-4} M EDTA Solutions.	95
4.02	Determination of the Ratio of the Conditional	

	Equilibrium Constants ($K'_{GdY^-}/K'_{CdY^=}$) for Gadolinium Nitrate and Cadmium Nitrate Solutions.	I07
4.03	Determination of ($K'_{MY^{+n-4}}/K'_{CdY^=}$) where MY^{+n-4} is GdY^- , NdY^- , SmY^- and $ZnY^=$ for Various Ratios of $C_{Cd^{+2}}/C_{M^{+n}}$.	I09
4.04	Data from the Titration of 1.710×10^{-4} moles of Sm^{+3} with 1.086×10^{-4} moles of Cd^{+2} as the indicator ion and EDTA as the titrant.	II2
4.05	Summary of Results of Amperometric Titrations of Gd^{+3} , Nd^{+3} , Sm^{+3} and Zn^{+2} using Cd^{+2} as the Amperometric Indicator and EDTA as the Titrant.	II7
4.06	Calculated Values of $\beta_{Cu^{+2}}$, $\beta_{CuY^=}$, $\beta_{Ca^{+2}}$, $\beta_{CaY^=}$, $\alpha_{Y^{-4}}$ and $\log (K'_{CaY^=}/K'_{CuY^=})$ for 2.2 M, 1.1 M and 0.5 M. NH_3 .	I29
A1.01	Results of Amperometric Titrations of Gd^{+3} , Nd^{+3} , Sm^{+3} and Zn^{+2} using Cd^{+2} as the Amperometric Indicator and EDTA as the Titrant.	I39

LIST OF FIGURES

Page

FIGURE

- | | | |
|------|--|----|
| 1.01 | Shapes of selected amperometric titration curves. | 8 |
| 1.02 | The conditional stability constants for scandium, mercury, copper and zinc ions with EDTA as a function of pH. | 13 |
| 1.03 | Idealized amperometric titration curve for a titration in which an electroactive substance, added as an amperometric indicator, forms a complex of less stability with the titrant than does the metal ion to be determined. | 17 |
| 1.04 | Possible shapes of photometric titration curves for reactions involving the formation of complexes. | 19 |
| 2.01 | Amperometric titration with an amperometric indicator. | 26 |
| 2.02 | Theoretical titration curves for the titration of M^{+n} using Ind^{+x} as the indicator ion, in the case where $K'_{MT}{}^{+n}$ is larger than $K'_{IndT}{}^{+x}$. | 27 |
| 2.03 | Conductometric titration of KCl with $NaClO_4$. | 29 |
| 2.04 | Curves for the titration of 1.0 moles of M^{+n} using 0.4 moles of Ind^{+x} as the indicator ion, in coordinates of moles of indicator ion unreacted versus moles of titrant added. | 35 |

2.05	Example of the program in Fortran language to calculate the titration curves for various ratios of conditional equilibrium constants and various concentrations of metal ion and indicator ion.	42
2.06	Correction graph for the application of the theoretical slope method of end point detection.	45
3.01	Figures for obtaining of statistical data on the effect of α , ϕ and Δ on end point precision using the extrapolation procedure.	56
3.02	Example of measurement technique.	57
3.03	Schematic representation of factors contributing to reading error.	59
3.04	Dependence of reading error, ΔM_{α} , on the angle between the extrapolated lines.	61
3.05	Dependence of reading error, ΔM_{α} , on the length of the segment of the line in region 2 that is available for extrapolation purposes.	64
3.06	Dependence of ΔL on the length of the segment of the line in region 2 that is available for extrapolation purposes.	65
3.07	Computer calculated points used for the statistical investigation of the effect of the ratio of the conditional equilibrium constants on the precision and accuracy of the extrapolation method of end point detection.	66

3.08	Schematic representation of the distance to be measured on each part of Figure 3.07.	67
3.09	Schematic representation of the precision of one end point determination by the theoretical slope method.	71
3.10	Comparison of the accuracy of the end points obtained by the two extrapolation techniques and the theoretical slope method.	73
3.11	Comparison of the precision of the end points obtained by the two extrapolation techniques.	74
4.01	Equilibria of thorium and copper with EDTA, hydrogen ion, hydroxyl ion, and chloro-acetate ion.	84
4.02	Amperometric titration apparatus for the determination of thorium using Copper (II) as the amperometric indicator.	89
4.03	Current voltage curve of 7.8×10^{-5} M Copper (II) and 7.1×10^{-4} M thorium solution.	91
4.04	Plot of Cu (II) diffusion current versus mole ratio of EDTA to Cu (II).	92
4.05	Current voltage curves of copper and thorium at pH of 3.1.	93
4.06	Titration curves of 1.66 milligrams of thorium with 4.461×10^{-3} M EDTA.	96
4.07	Titration cell used for amperometric titrations and equilibrium constant determinations using a dropping mercury electrode.	101

- 4.08 Current voltage curves for Cd^{+2} and Zn^{+2}
at $\mu = 0.1$ and $p_a\text{H} = 4.2$. 103
- 4.09 Expanded correction graph for the theoretical
slope method of end point detection in the
range of high percent of indicator ion reacted. 114
- 4.10 Typical titration curves of gadolinium and
neodymium. 116
- 4.11 Titration of 5.58×10^{-4} moles of Ca^{+2}
and 2.43×10^{-4} moles of Cu^{+2} using EDTA as
the titrant. $[\text{NH}_3] = 2.2 \text{ M}$. 121
- 4.12 Titration of 5.58×10^{-4} moles of Ca^{+2}
and 2.43×10^{-4} moles of Cu^{+2} using EDTA
as the titrant. $[\text{NH}_3] = 1.1 \text{ M}$. 122
- 4.13 Titration of 5.58×10^{-4} moles of Ca^{+2}
and 1.46×10^{-4} moles of Cu^{+2} using EDTA as
the titrant. $[\text{NH}_3] = 0.6 \text{ M}$. 124
- 4.14 Titration curve for Ca^{+2} and Cu^{+2} using EDTA
as the titrant. $[\text{NH}_3] = 0.5 \text{ M}$. 125
- 4.15 Dependence of the ratio of K'_{CaY^-} to K'_{CuY^-} on
the concentrations of ammonia. 126

PRINCIPAL SYMBOLS


i_d	average diffusion current in microamperes.
K	thermodynamic equilibrium constant.
K'	conditional equilibrium constant.
A	Absorbance.
C_M^{+n}	total concentration of the metal ion not complexed with the titrant.
C_{Ind}^{+x}	total concentration of the indicator ion not complexed with titrant.
C_T	total concentration of uncomplexed titrant.
C_{IndT}^{+x}	total concentration of indicator ion complexed with titrant in the ratio of 1:1
C_{MT}^{+n}	total concentration of metal ion complexed with titrant in the mole ratio of 1:1.
α	acute angle between extrapolated lines.
Δd	band of uncertainty as defined on page 59 .
ΔL	band of uncertainty of extrapolated line as defined on page 59 .
ΔM_α	uncertainty of a measurement.
ϕ	length of the segment of the line that is available for extrapolation purposes.
σ	standard deviation
E°	standard potential in volts.
α_4	fraction of free EDTA present as the aquated ion.
β_M^{+n}	fraction of metal ion not complexed with titrant T.
β_{MT}^{+n}	fraction MT^{+n} that is present as the aquated species.

1. INTRODUCTION

Most amperometric and photometric titrations can be carried out by measurement of the current or light absorbing properties of the titrant, substance to be titrated, or a complex of both. In some cases such measurements are not feasible. In some of these cases a metal ion species exhibiting such measurable properties

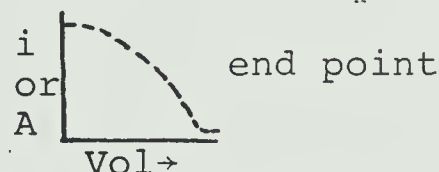
may be added to act as a so-called amperometric or photometric indicator. When amperometric or photometric indicators are used and favorable equilibria exist,

reliable end points can be obtained by the



The graph shows a horizontal dashed line at a high current level (labeled 'i or A' on the y-axis) that drops sharply to a lower current level at a specific volume (labeled 'Vol' on the x-axis). The drop is represented by a dashed line.

straightforward extrapolation method. When equilibria conditions become unfavorable,



location by extrapolation is difficult because of curvature in the end point region. There has been concern in the literature over this curvature. The work in this thesis is primarily concerned with end point location under these difficult conditions.

The accuracy and precision limitations of the extrapolation method of end point detection as applied to titrations using metal indicator ions have been investigated. Factors that influence the precision of the extrapolation method have also been examined. A

new method of end point detection is proposed that enables end points to be found under unfavorable equilibria conditions. A comparison of the accuracy and precision of this method with that of the extrapolation method is made. Experimental data are presented to illustrate the applicability of the two methods.

In this first chapter, descriptions of the theory and background of amperometric and photometric titrations have been presented in addition to descriptions of amperometric and photometric indicators.

1.01

AMPEROMETRIC TITRATIONS

Measurement of current may be used to follow the concentration changes during a chemical or electrochemical reaction. It may be used to follow the course of a titration, and in particular to determine its end point. Such titrations are called amperometric titrations and may be volumetric or coulometric depending on whether the reactant is added in known amounts from a buret or by means of electrolysis.

The apparatus for an amperometric titration consists of two electrodes, usually one indicator electrode and one reference electrode. The indicator electrode is often a dropping mercury electrode (D.M.E.) or a solid microelectrode such as a rotating platinum electrode (R.P.E.). Stock(1) provided a comprehensive outline of the various types of microelectrodes that have been used. The reference electrode is usually a saturated calomel electrode (S.C.E.). A constant voltage is applied across the two electrodes, either by using a reference half cell with an appropriate potential or a S.C.E. at a constant potential. In either case the current passing through the cell is measured with a sensitive microammeter.

The current is measured at a potential in the

diffusion current region of the current voltage curve. In this region, the current is independent of the potential of the indicator electrode because a limiting case of concentration polarization exists at the indicator electrode. At potentials in the diffusion current region, the concentration of reducible material at the electrode surface undergoing electrochemical reaction is maintained at a value essentially zero. The observed current is therefore limited by the rate at which the electroactive material is supplied to the electrode surface by diffusion. The rate of diffusion and hence the current, is proportional to the concentration of the diffusing substance in the bulk of the solution. For a D.M.E. the relation between diffusion current and concentration is given by the Ilkovic equation (2)

$$i_d = 607 \, n \, D^{\frac{1}{2}} C m^{\frac{2}{3}} t^{\frac{1}{6}} \dots \quad (1.01)$$

where i_d is the average diffusion current in micro-amperes; n , the number of faradays per mole of electrode reaction; D , the diffusion coefficient in cm^2/sec ; C , the concentration of diffusing species in millimoles/liter; m , the rate of flow of mercury in mg./sec. ; t , the drop time in seconds. Equation 1.01 indicates that there is a linear relation between diffusion current and concentration.

Experimentally, it has been found(3) that the drop time is dependent on the potential and the solvent used. In reporting data obtained with a D.M.E. it is conventional to record the values of the drop time and the quantity $m^{2/3}t^{1/6}$ under the experimentally used conditions. Corrections due to the changing value of $m^{2/3}t^{1/6}$ are important in the interpretation of current voltage curves. The diffusion coefficient is dependent on a number of factors such as solvent properties, nature of inert ions present, and ionic strength (μ). For these reasons all data reported must include the temperature used and measurements are usually carried out in a constant temperature bath.

Since amperometric titrations are performed at a fixed potential difference between the two electrodes, the corrections arising from the dependence of $m^{2/3}t^{1/6}$ on potential are not involved.

The sensitivity of the D.M.E. is limited only by the size and reproducibility of the residual current. Under normal experimental conditions the precision of the polarographic method is of the order of 1% in the concentration range from 10^{-2} M down to about 10^{-4} M, and 5% between 10^{-4} and 10^{-5} molar. The lower limit of polarographic detection is in the neighborhood of 10^{-6} M.

At constant temperature, the limiting current obtained at a stationary microelectrode depends upon: the

characteristics of the microelectrode, the properties of the substance undergoing reaction at the electrode and, the concentration of the electroactive substance in the solution. The microelectrode characteristics and the properties of the electroactive substance should remain constant during a particular experiment. The relation between current and concentration should then be

$$i_d = k \times C \quad (1.02)$$

where k is a constant dependent on the characteristics of the microelectrode, the properties of the substance undergoing reaction at the electrode, and the nature of the solution.

Constancy of temperature is particularly important both to avoid thermal convection and because the current increases about 4% per degree rise in temperature(4). With proper care however, a precision of about 1% can be obtained in diffusion current measurements.

Several workers(5,6,7)investigated the relation between the rate of electrode rotation of a R.P.E. and the limiting current given by various reducible species. Ferret and Phillips found the generally applicable relation,

$$\text{Limiting current} = K \times (\text{RATE of ROTATION})^x \dots (1.03)$$

where K is a constant. The value of the exponent x varied with the ion. For example, silver ion gave the highest value, 0.67, and oxygen the lowest, 0.27.

They interpreted their results to indicate correlation between the value of x and the degree of reversibility of the electrode reaction.

By using a rotating electrode, the diffusion layer thickness is decreased. The concentration gradient, $(\frac{\partial C}{\partial x})$, is thereby increased, resulting in currents 10 to 100 times larger than with a D.M.E. The larger currents attained allow correspondingly smaller concentrations to be measured without loss of precision. However, there are limitations to the more universal use of the R.P.E. because the discharge of hydrogen may interfere in some cases at negative potentials. In these cases, a D.M.E. with its larger value of hydrogen overpotential may be used. On the other hand, the oxidation of mercury limits the anodic range of the D.M.E., and in some of these cases the rotating electrode extends the useful range in the positive direction to about +0.9 volts versus the S.C.E. at which point the oxidation of water to oxygen begins. The shapes of the various types of titration curves that may be obtained are shown in Figure 1.01(8) and are classified in TABLE 1.01(8). Curves Q and R give the most precise while curves S and T give the least precise end points. However, curves P, Q, M and N are the types of titration curves most often obtained.

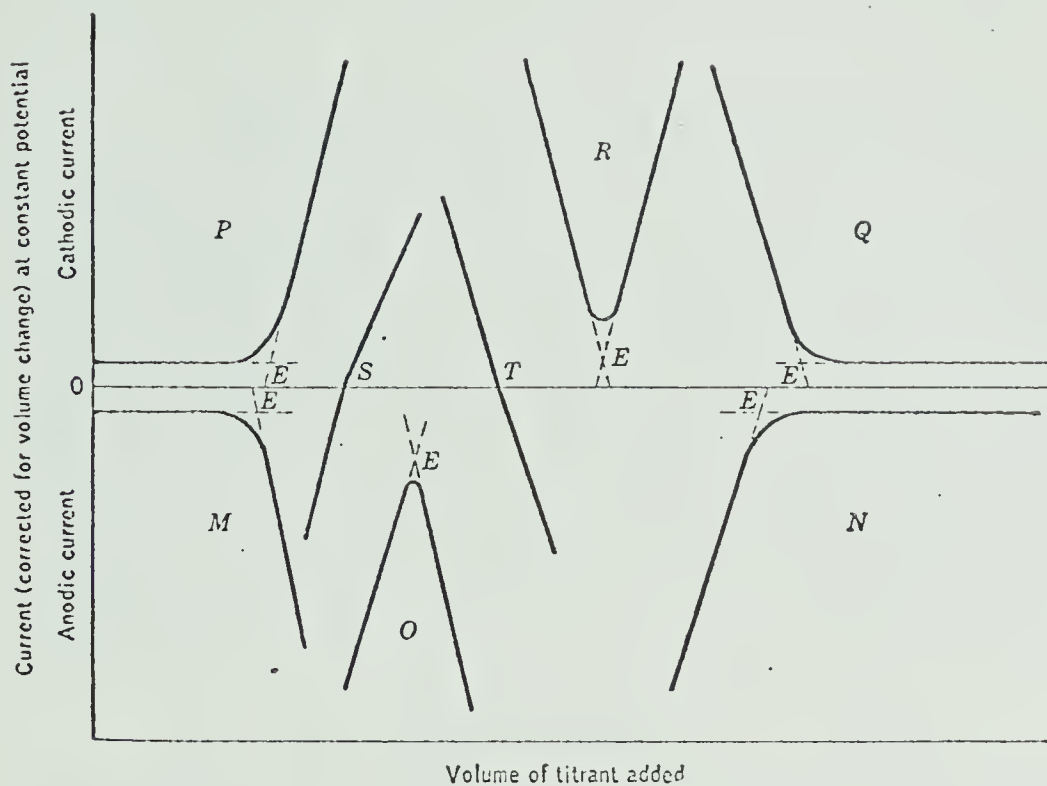


Figure 1.01 Shapes of selected idealized amperometric titration curves. E is the end point of each. (Copied directly from Jordan and Clausen (8)).

Experimentally, the addition of the titrant dilutes the solution in the titration cell. This causes the current readings to be lower than they would otherwise be and the straight line portions of the titration curve deviate more from linearity. In such cases, the current should be corrected for dilution by multiplying it by the factor $(V + v/V)$. V is the volume of the solution being titrated and v is the volume of reagent added. The use of a reagent, which is considerably more concentrated (by a factor of 10 to 20) than the solution being titrated makes the corrections for dilution negligible and permits one to ignore it.

Table 1.0]. Electrochemical Behaviors of Reactants Corresponding to Various Types of Amperometric Titration Curves

The letters appearing in the first column of this table denote the various types of amperometric titration curves which are sketched and identified by the same letters in Fig. 1.0]. In the headings of the remaining columns, the symbol "R" refers to the electroreducibility, and "O" to the electrooxidizability, of the substance in question at the constant potential used in the titration. In the body of the table, a + means that the substance referred to is electroreducible under the conditions of the titration if it appears in a column headed "R," or electrooxidizable if it appears in a column headed "O," whereas a - means that the substance is not reducible or oxidizable, respectively, under these conditions. For example, the first line of the table means that a curve having the shape identified as *M* in Fig. 1.0] will be obtained if a substance that can be neither oxidized nor reduced at the potential selected is titrated with a reagent that can be oxidized but not reduced. Multiple entries bearing the same identifying letter denote alternative ways in which the same type of titration curve may be obtained.

Curve type	Reagent		Substance titrated		Indicator			
	R	O	R	O	Added <i>ab initio</i>		Generated <i>in situ</i>	
					R	O	R	O
<i>M</i>	-	+	-	-
<i>M</i>	-	-	-	-	-	+
<i>N</i>	-	-	-	+
<i>O</i>	-	+	-	+
<i>O</i>	-	-	-	+	-	+
<i>P</i>	+	-	-	-
<i>P</i>	-	-	-	-	+	-
<i>Q</i>	-	-	+	-
<i>Q</i>	-	-	-	-	+	-
<i>R</i>	+	-	+	-	+	...
<i>R</i>	-	-	+	-	+	-
<i>S</i>	+	-	-	+
<i>T</i>	-	+	+	-

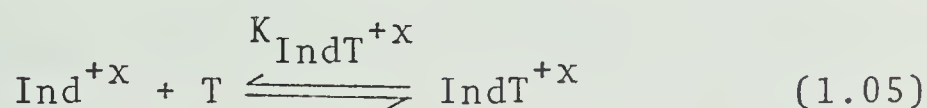
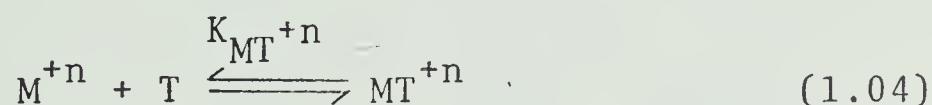
(Copied directly from Jordan and Clausen (8)).

1.02

AMPEROMETRIC INDICATORS

The types of amperometric titration curves illustrated in Figure 1.01 are those in which either the species to be determined or the reagent or both are electroactive. In some cases (9,10) where neither the reagent or reactant can be reduced or oxidized, the titration may be carried out by addition of an appropriate metal ion species, which is electroactive, to the solution which is to be titrated. This metal ion is called an amperometric indicator. The indicator must give a diffusion current at the potential chosen and must react with the titrant, usually less readily than the substance to be determined.

For example, consider the general case of the complexometric titration of a metal ion, M^{+n} , in the presence of an indicator metal ion, Ind^{+x} , with a titrant T. The main reactions would be

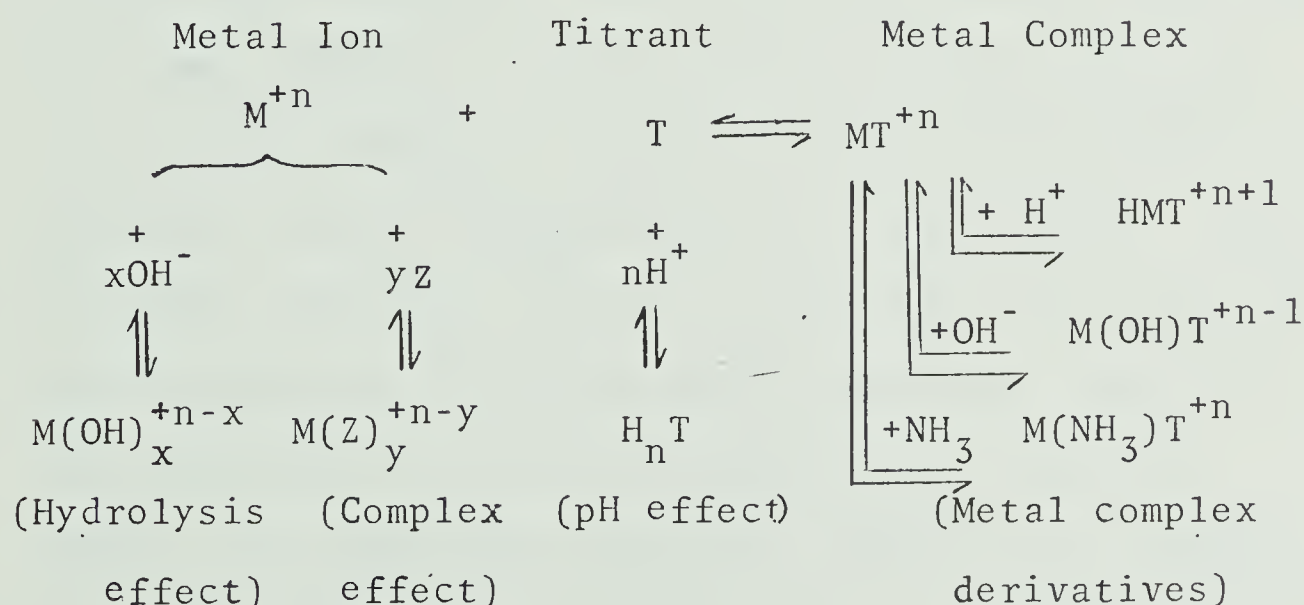


The concentration stability constants of the two metal complexes are given by

$$K_{MT^{+n}} = \frac{[MT^{+n}]}{[M^{+n}][T]} \quad \text{and} \quad K_{IndT^{+x}} = \frac{[IndT^{+x}]}{[Ind^{+x}][T]} .$$

where $[M^{+n}]$ is the concentration of the aquated M^{+n} ion, $[\text{Ind}^{+x}]$ is the concentration of the aquated indicator ion, $[MT^{+n}]$ and $[\text{IndT}^{+x}]$ are the concentrations of the metals complexed with T only. It should be realized that the metal ions, whether complexed or not, are unlikely to exist simply as ions such as M^{+n} (aquated) or IndT^{+x} (aquated) in any appreciable concentration. Thus the concentration stability constant is not the best criterion of the extent of metal complex formation.

There are other equilibria to be considered. For example, the various competitive equilibria involving M^{+n} and T are summarized as follows



Consideration of these competitive equilibria gives a conditional stability constant (11, 12, 13, 14), K'_{MT} which takes into account the effect on the $M^{+n} + T \rightleftharpoons MT^{+n}$ equilibrium of hydrolysis, pH and any other side reactions that may occur such as reaction of M^{+n} with the buffer. The conditional equilibrium constant is therefore more informative than the concentration stability constant.

In recent times, the most popular titrants are those such as ethylenediaminetetra-acetic acid (EDTA) and nitrilotriacetic acid (NITA), which form chelate rings with metal ions. Such chelons are proton acceptors and the hydronium ion competes with the metal ions for the chelating agent, thereby reducing the effective stability of the metal chelate. For this reason, metal ions which form weak complexes can be titrated effectively only in alkaline solution. Metal ions which form stable complexes can be titrated even in acid solution. This pH effect indicates the use of alkaline conditions for the formation of the most stable complexes. However, the hydrolysis of metal ions under such conditions lowers the conditional stability constant and counteracts the improvement resulting from an increase in pH. This generally results in maximum complex chelate stability at an intermediate pH, but the stability at this pH is lower than the concentration stability constant. Figure 1.02 shows the conditional stability constants for mercury, copper, zinc and scandium ions with EDTA plotted as a function of pH.

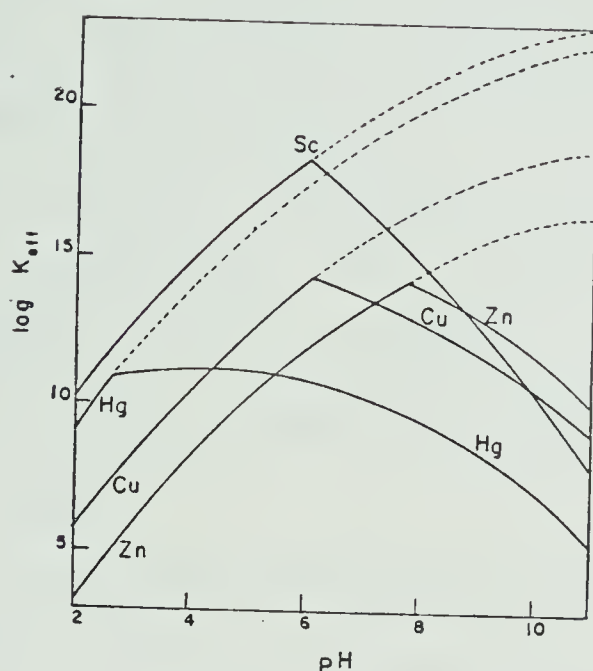


Figure 1.02 The conditional stability constants for scandium, mercury, copper and zinc ions with EDTA as a function of pH. (From Reilley and Schmidt, J. Chem. Ed., 36, 555 (1959)).

In this figure the conditional stability constant for the copper-EDTA chelate has a value of 10^6 at a pH of 2 and a value of about 10^{10} at a pH of 11. The maximum conditional constant occurs at a pH of 6 where a value of 10^{14} is obtained. Similarly, maximum conditional stability constants of 10^{11} at a pH of 2.5 for mercury, 10^{18} at a pH of 6 for scandium, 10^{14} at a pH of 8 for zinc are obtained. Ringbom (13) reports values of $10^{18.8}$, $10^{21.8}$, $10^{23.1}$ and $10^{16.5}$ for the concentration stability constants of the copper, mercury, scandium, and zinc, complexes with EDTA, respectively at $M = 0.1$.

The variation in conditional stability constants with pH often permits selective titrations, using appropriate pH adjustments. For example, a metal (such as thorium) forming a stable complex can be titrated in the presence of one (such as copper) forming a weaker complex by the use of acidic conditions. In a similar manner auxiliary complexing agents, such as a buffer or a masking agent, can also react with the metal ion and decrease the conditional constant.

Under certain pH conditions the metal complex may react with OH^- or H^+ to form complexes that may be written as MTH^{+n+1} or M(OH)T^{+n-1} . Some metal complexes also form derivatives of the type MXT where X may be substances such as NH_3 , Cl^- or CNS^- . These reactions have the effect of increasing the conditional stability constant.

Since an amperometric titration involves a complex reaction of the titrant with both the metal, M^{+n} , to be determined and the indicator metal, Ind^{+x} , the above mentioned factors must be considered for both individual equilibria. The greater the value of $K'_{\text{MT}}^{+n} / K'_{\text{IndT}}^{+x}$ the more precise will be the amperometric titration. Also, knowledge of the values of the conditional stability constants for the metal ion complex and the indicator ion complex and the factors upon which they depend is often helpful in the choice of a suitable amperometric indicator. Calculated values of the conditional stability constants can be no more precise than

the data from which they are calculated. Often the available data have appreciable uncertainty, and for some equilibria, notably those involving chelonate derivatives, no data at all are available. For this reason, a precise knowledge of the conditional stability constants can only be obtained by experimentation.

As mentioned earlier, if a metal ion is to be determined amperometrically and it, as well as the titrant, is not electroactive, an amperometric indicator that yields a diffusion current at a suitable potential must be chosen. The indicator ion must react with the titrant, but less readily than the metal ion to be determined. Ideally under these conditions, the metal ion would react with the titrant until it is all complexed, then the titrant would complex with the indicator ion. At this point the diffusion current due to the electrochemical reaction of the indicator ion would decrease until all the amperometric indicator has been complexed. A titration curve of the shape shown in Figure 1.03 would be expected.

There are two end points in amperometric titration curves obtained using amperometric indicators. Most commonly the end point corresponding to point A in Figure 1.03 is employed and it corresponds to the amount of metal ion to be determined. A second end point corresponding to point B has been used in some cases. Point B corresponds to the amount of the metal ion determined plus the amount of indicator ion. Using this end point the amount of the metal ion to be

determined can be calculated from a knowledge of the amount of indicator ion initially present.

The extent of curvature in the region near point A is dependent on the size of the ratio of the conditional equilibrium constant of the metal to be determined - titrant complex to the conditional equilibrium constant of the amperometric indicator - titrant complex.

The curvature in this region is discussed at length in a following section but, in general, as the ratio of the constants decreases, the amount of curvature increases and as a result the ability to detect the first end point decreases. The curvature in the region of point B is dependent on the size of the conditional equilibrium constant of the indicator ion- titrant complex.

In the cases where the size and ratio of the constants are both large, as in Figure 1.03, either end point can be found with high precision by extrapolation. In the special case where the ratio is unity the second end point can be located precisely by extrapolation whereas the direct location of the first end point is impossible by this method. Undoubtably in some cases the location of the second end point would be preferable. However to keep the scope of this study within manageable limits, it has been arbitrarily confined to a critical evaluation of the characteristics and limitations of the more commonly used end point corresponding to point A in figure 1.03.

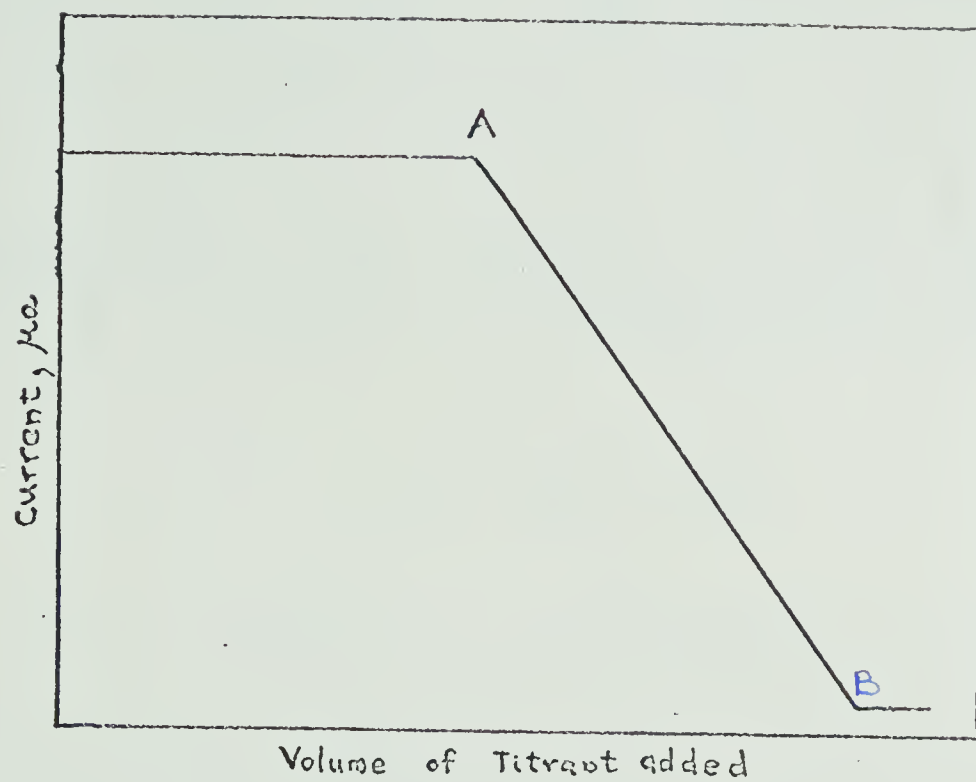


Figure 1.03 Idealized amperometric titration curve for a titration in which an electroactive substance, added as an amperometric indicator, forms a complex of less stability with the titrant than does the metal ion to be determined.

1.03

PHOTOMETRIC INDICATORS

For the determination of titration end points, the quantitative measurement of light absorption can be used in a manner somewhat analogous to that of current measurements in amperometric titrations. The fundamental law of monochromatic light absorption, on which photometric titrations are based, is the Bouguer-Lambert-Beer Law(15).

$$A = - \log T = abc$$

where A is absorbance; T, transmittance; a, absorptivity; b, path length of light through absorbing medium; and c, concentration of the light-absorbing constituent. The most important consequence of this law is that absorbance is directly proportional to the concentration of the absorbing ions. This means that in a titration in which the titrant, the reactant, or the product absorbs, the plot of absorbance versus titrant added will consist, if the reaction is complete, of two straight lines intersecting at the end point. In this respect, photometric titrations are similar to amperometric titrations.

The shape (16)of a photometric titration curve will be dependent on the light-absorbing properties of the reactant, titrant and products of the reaction at the wavelength (λ) used. Figure 1.04a illustrates the

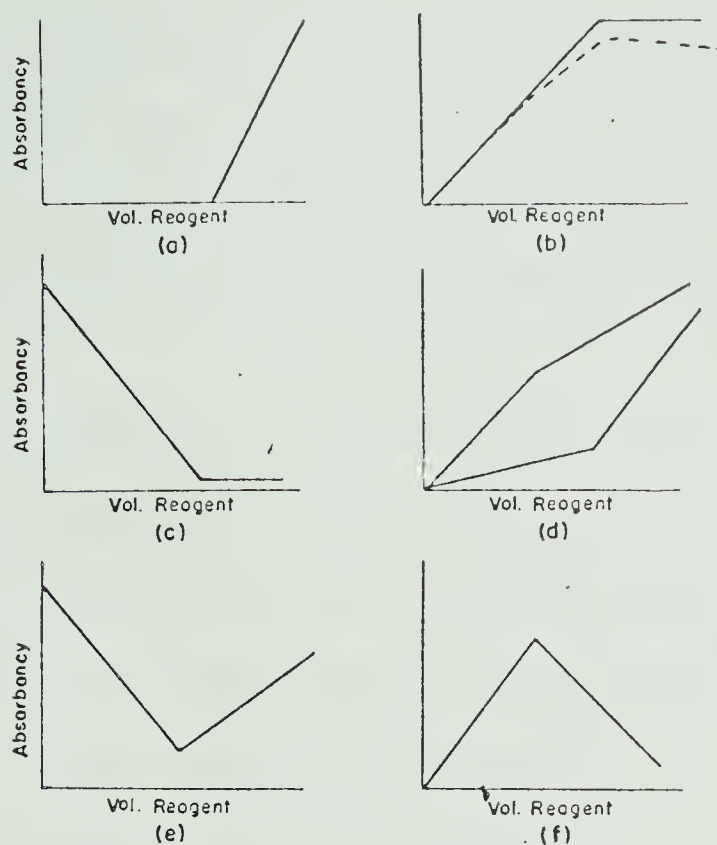


Figure 1.04 Possible shapes of photometric titration curves for reactions involving the formation of complexes. (Taken directly from Goddu and Hume, *Anal. Chem.*, 26, 1740 (1954)).

titration curve to be expected where only the reagent absorbs light. Figure 1.04b is characteristic of systems where only the product of the reaction absorbs and Figure 1.04c, of systems where the absorbing substance titrated is converted to a nonabsorbing product. When a colored reactant is converted to a colorless product by a colored reagent, curves similar to Figure 1.04e, are obtained. Curves d and f might represent the consecutive addition of ligands to form two successive complexes of differing absorption.

As in an amperometric titration, the extrapolation of the straight line portions of the photometric curve enables one to locate the end point without relying on the uncertain data taken in the vicinity of the equivalence point.

Earlier workers (17,18,19,20) plotted transmittance or a quantity proportional to it, such as photocell output, rather than absorbance, against volume of titrant. Under the proper conditions a curve similar to a potentiometric titration curve is obtained. This type of plot has the advantages inherent in the use of the inflection point to locate the end point of a titration but where the changes in reading near the end point are not large the use of absorbance is preferable.

In photometric titrations, where neither the metal to be determined, the titrant nor product of the reaction absorb light, the titration may be carried out by use of an auxiliary reagent which does. This auxiliary substance is called a photometric indicator. It must absorb light at an appropriate wavelength and in general react with the titrant after the main product has been formed.

1.04 COMPARISON OF TITRATION SYSTEMS INVOLVING AMPEROMETRIC AND PHOTOMETRIC INDICATORS.

As stated previously, for a metal ion to be an effective amperometric or photometric indicator it must form a complex with the titrant of lower stability than the metal to be determined. For a successful amperometric indicator there is the further requirement that the indicator ion be more easily reduced than the metal ion to be titrated and more easily reduced than the foreign ions that may interfere electrochemically. Ions that are reduced at more positive potentials will give a large background current and cause poor precision.

For a successful photometric indicator there is similarly the requirement that only the indicator ion absorb at some appropriate wavelength. Interferences that absorb light at higher or lower wavelengths will not interfere with the absorbance measurements due to the indicator ion. When light absorption is used there is the freedom of choice that either the concentration of the indicator ion-titrant complex or the indicator can be measured. Absorption due to the indicator ion will in general not occur at the same wavelength as absorption due to the indicator ion-titrant complex. In contrast, in an amperometric titration, one does not have the freedom to use the

indicator ion-titrant complex as a means of following the titration because the indicator ion will be more easily reduced than the complex and will interfere with the diffusion current due to the reduction of the complex of the titrant with the indicator ion.

In the diffusion limited region of a current-voltage curve the current is constant and is not affected by the potential chosen. For this reason, a small variation in potential during a titration will not affect the measurements of the diffusion current. However, the absorption of light by an indicator has a maximum value at a particular wavelength and decreases in value as the wavelength becomes larger or smaller. Due to the dependence of absorbance on wavelength, absorption measurements will vary with small changes in it, and measurements should be made at maximum absorbance rather than at wavelengths where absorption is changing rapidly.

As was previously discussed (Section 1.01), the range in which a metal ion may be reduced using a D.M.E. is limited by mercury oxidation in the positive potential direction and by hydrogen discharge in the negative direction. The choice of a proper indicator electrode such as a R.P.E. extends the range in the positive direction.

The wavelength at which a metal ion may absorb light is often complicated by the solvent. This may be remedied only by use of a solvent which does not itself absorb at the wavelength that the indicator ion absorbs.

For photometric titrations, stirring must not be sufficiently turbulent to draw air into the solution and in this way interfere with the photometric readings. In amperometric titrations using a R.P.E. such turbulence does not interfere and the only requirement is that the rate of rotation of the electrode be constant. Of course, with a D.M.E. stirring must be avoided and even vibrations or thermal convection will affect the current readings.

2. END POINT DETECTION IN AMPEROMETRIC AND PHOTOMETRIC TITRATIONS WITH UNFAVORABLE EQUILIBRIUM CONSTANTS.

In this chapter a summary of methods presently used for end point detection are presented. The extrapolation method of end point detection in systems employing amperometric or photometric indicators is first discussed. Following this is a brief summary of methods of end point detection that involve calculation. Next is a description of the theory and applicability of a proposed method of finding the end point in titrations where the extrapolation method is not feasible. The relation of the proposed method to the conditional equilibrium constants has been described in addition to correction factors and how they are obtained. Finally a recommended procedure for the application of the proposed method is presented.

2.01 THE EXTRAPOLATION METHOD OF END POINT DETECTION AS APPLIED TO THE FIRST END POINT.

In general, the detection of an accurate and precise end point in a titration requires that several minimum requirements be met. For example, the rate of the reaction must be fast, the stoichiometry must be known and definite and the equilibrium constants must be large enough to allow satisfactorily complete reactions. The minimum equilibrium constant requirement depends on the

method used to obtain titration data and the procedure used to detect the end point. For example, in the titration of equal concentrations of a sought after ion and an interfering ion using a visual indicator, the equilibrium constant for the reaction involving the ion of interest must exceed that of the interfering ion by at least 10^5 to 10^6 . For a potentiometric titration under the same conditions, a difference of about 10^4 is necessary. For amperometric or photometric titrations employing metal indicator ions, the requirements are even less stringent. The shape of the amperometric and photometric titration curves and the precision of the end point measurements are dependent on the ratio of the equilibrium constants. The idealized amperometric titration curve illustrated in Figure 1.03 has a ratio of equilibrium constants that is approaching infinity and therefore no difficulty is encountered in locating the end point. From the point of view of curvature in the region of the end point as the ratio of the equilibrium constants decreases, the amount of curvature in the end point region will increase until a single straight line is obtained when the ratio becomes unity. These two extreme cases are illustrated in Figure 2.01.

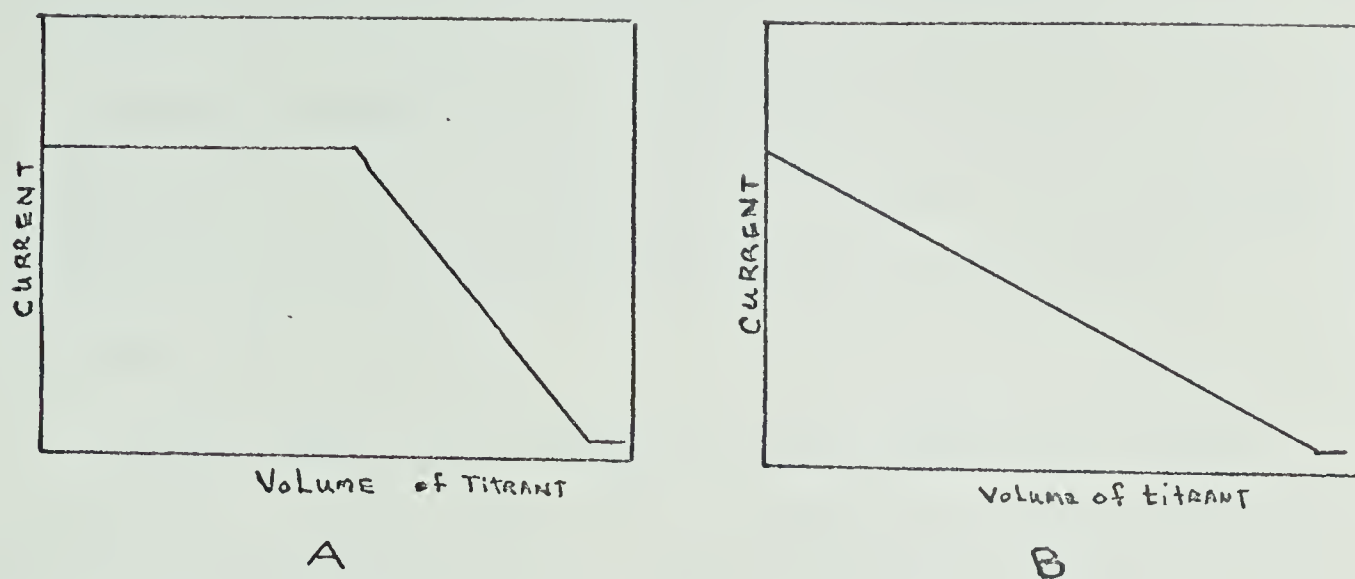


Figure 2.01 Amperometric titration with an amperometric indicator.
 A - Ratio of conditional equilibrium constants equal to infinity.
 B - Ratio of conditional equilibrium constants equal to unity.

A curve of the type shown in curve A would be obtained for a large ratio of equilibrium constants and a curve of the type shown in curve B for a ratio equal to one.

To detect end points in titration curves of the type illustrated by A, the extrapolation or tangent method is generally used, which unfortunately loses its effectiveness when the ratio of equilibrium constants becomes less than about 100(21). When the ratio is 100, 1% of the substance with the smaller equilibrium constant (amperometric indicator) will have reacted at the point where one half of the substance with the larger equilibrium constant has reacted.

Several workers have developed mathematical treatments for cases in which simple extrapolation of two straight lines to their intersection is unsatisfactory as a means of detecting an end point. This section is confined to a brief discussion of only the extrapolation method and the mathematical approach is discussed in the following section.

In the specific titration curves shown in Figure 2.02 where a metal ion, M^{+n} , is titrated in the presence

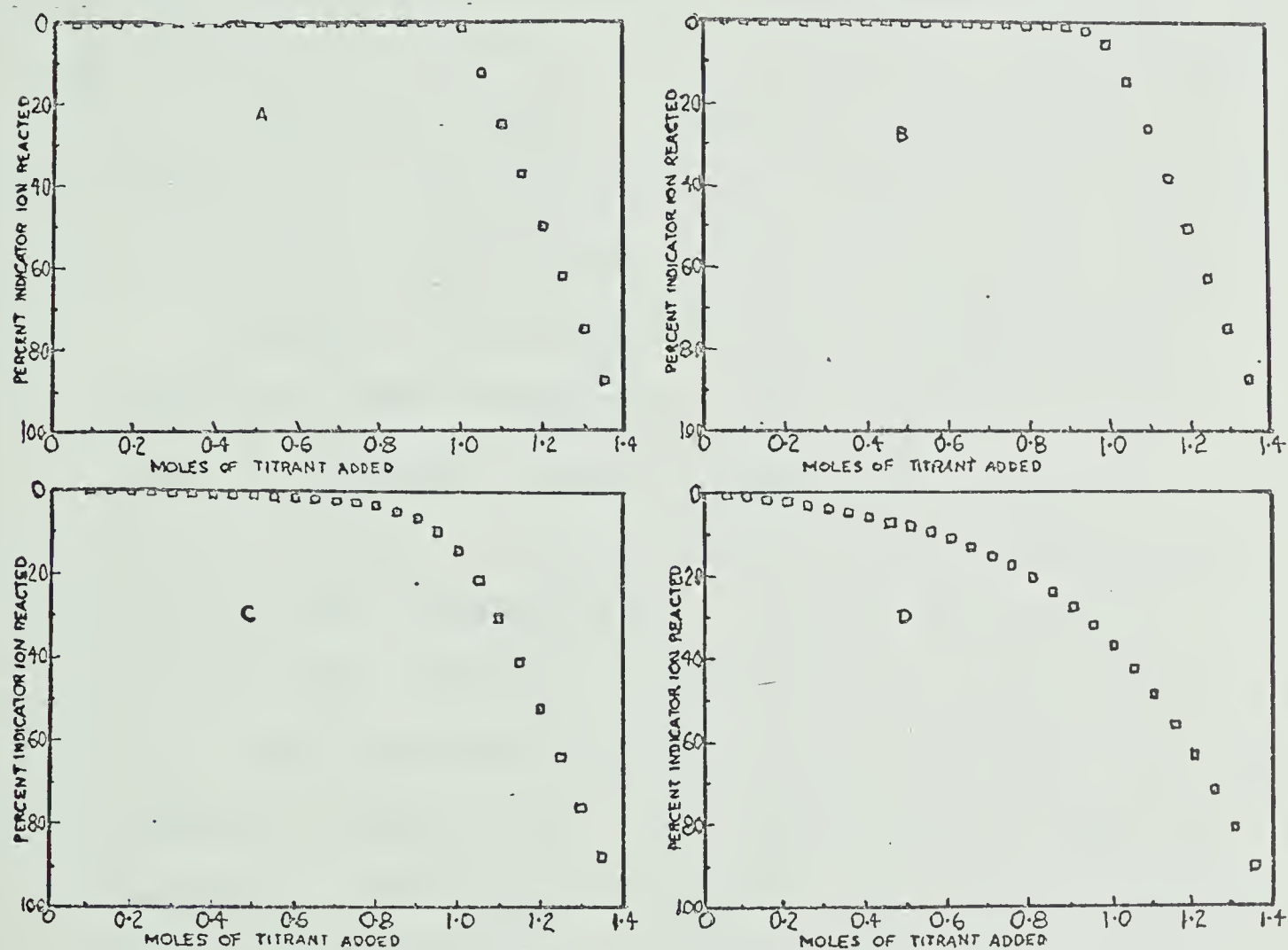


Figure 2.02 Theoretical titration curves for the titration of M^{+n} using Ind^{+x} as the indicator ion, in the cases where K'_{MT}^{+n} is larger than K'_{IndT}^{+x} . Curves A, B, C and D correspond to $\log(K'_{MT}^{+n}/K'_{IndT}^{+x})$ values of 4.0, 3.0, 2.0, 1.0. The initial amounts of M^{+n} and Ind^{+x} in each case is 1.0 and 0.4 moles.

of a metal ion indicator, Ind^{+x} , the effectiveness of the extrapolation procedure decreases as the value of the ratio of the conditional equilibrium constants $\left(\frac{K'_{\text{MT}^{+n}}}{K'_{\text{IndT}^{+x}}}\right)$ approaches 1.0. In Figure 2.02A, for a ratio of $10^{4.0}$, no difficulty is encountered in choosing the linear portions to be used for extrapolation; whereas in Figure 2.02D, where the ratio has a value of 10, this choice is not obvious. In fact, there are no straight line portions of the curve to be extrapolated. In a following section, a method is proposed for the detection of end points in cases such as this, where the ratio of the equilibrium constants approaches unity.

Because the end point using the extrapolation method is found graphically, some attention must be given to choosing a large enough scale, so that it does not become a limiting factor in the precision of the end point determination. To show this effect, consider the following conductometric titration (22, 23). The experimental data are given in TABLE 2.01 and plotted in Figure 2.03. The theoretical end point is 2.19 mls. The values are plotted twice using different scales for the ordinate. Curve A gives an end point of 1.8 mls and curve B gives an end point of 2.2 mls. When the scale as large as in B is used, it becomes obvious that invalid data such as the last

TABLE 2.01 THE TITRATION OF KCl WITH NaClO_4 .(From C. Liteanu and D. Cörmös, *Talanta*, 7, 18 (1960)).

NaClO_4 , mls	\sqrt{n}	NaClO_4 , mls	\sqrt{n}	NaClO_4 , mls	\sqrt{n}
0.2	9.05	1.2	6.33	3.2	8.00
0.4	8.70	2.4	6.58	3.4	8.53
0.6	8.30	2.6	6.78	3.6	9.02
0.8	7.98	2.8	7.11	3.8	9.58
1.0	6.60	3.0	7.50	4.0	10.05

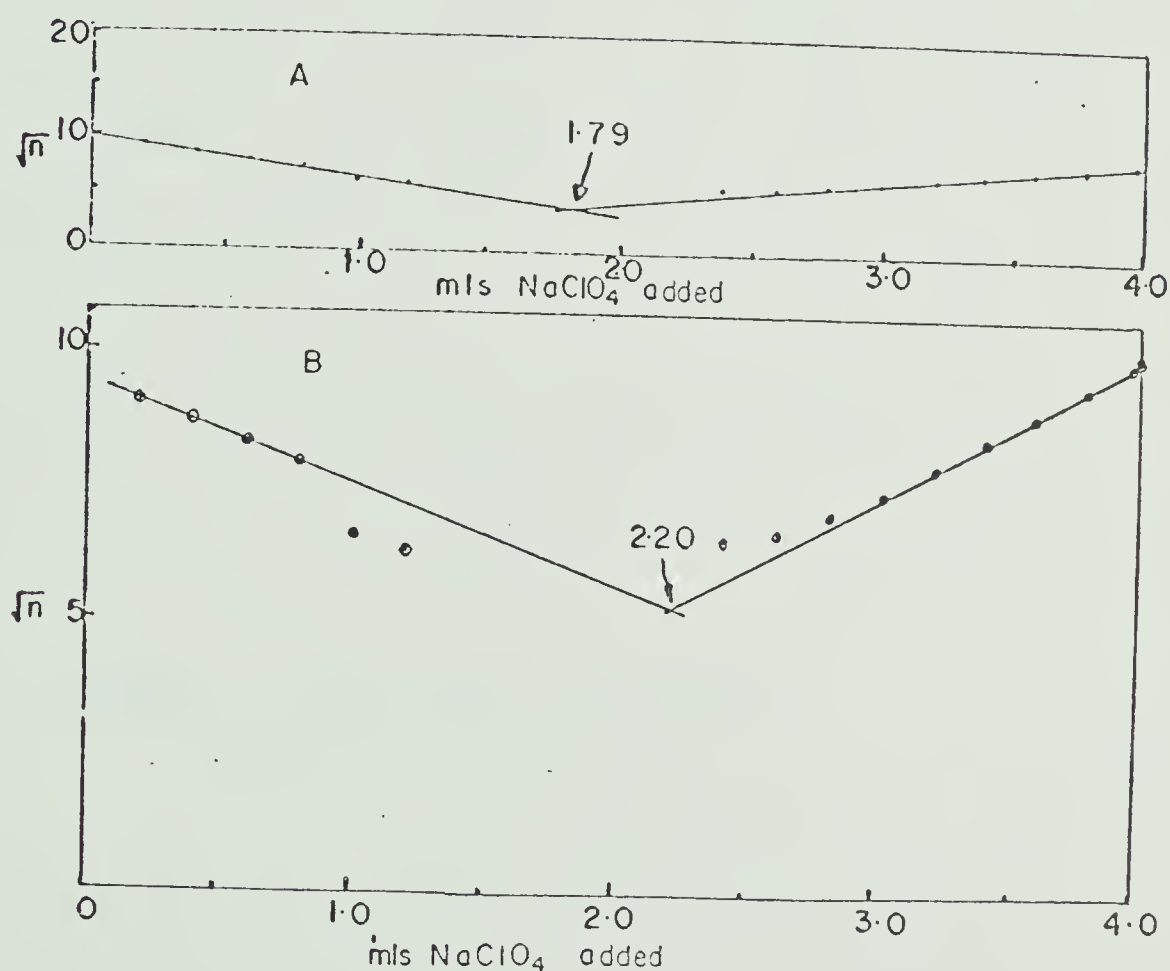


Figure 2.03 Conductometric titration of KCl with NaClO_4 .
 A - 1 unit of \sqrt{n} per 2 mm. of ordinate scale. B - 1 unit
 of \sqrt{n} per 1 cm. of ordinate scale.

two points before the end point should be omitted. In a similar way, Goddu and Hume (16) state that for systems where the straight line portions must be extrapolated from regions far from the end point, and a large portion of the curve must be plotted, then graph paper should be used which allows one to plot the curve on a large scale. For example, if the end point is in the vicinity of 100 to 150 divisions, estimation to half a division is equivalent to 0.5 percent relative precision.

The angle of intersection and the uncertainty of the individual points also affect the precision with which the end point may be located on a given type of graph paper. In general, the location of the intersection of two experimental lines with a sharp angle of intersection can be determined with better precision than when the angle of intersection is low. If one of the lines is a base line and therefore subject to less uncertainty, the uncertainty in the intersection will also be decreased.

2.02 METHODS OF END POINT DETECTION INVOLVING CALCULATION

Mathematical treatments of data as a means of detecting end points have been used to interpret conductometric, photometric and thermometric titrations but have

not generally been used in connection with amperometric titrations. One reason may be that many amperometric titrations involve precipitation, in which cases, precipitate separation and the approach to equilibrium is often slow. Under these conditions the current readings do not readily stabilize and little is to be gained by departing from the simple graphical method.

It should be noted that the rounding⁽²⁴⁾ of an amperometric precipitation titration curve is controlled by the ratio of K_{sp}/C_0 where K_{sp} is the solubility product and C_0 is the initial concentration of the species that is precipitated by addition of the titrant. If the ratio does not exceed 10^{-3} , the rounding will be small, so that the significant portions of the arms of the titration curve are linear. In such cases, the extrapolation method gives satisfactory results provided that the establishment of equilibrium is rapid, the temperature is constant so that solubility does not change, and the titration is continued well past the end point so that the last part of the titration curve becomes closely linear.

J. H. Boulard⁽²⁵⁾ developed a method of calculating the intersection of the lines by taking into account two points immediately before the end point and two points immediately after. This method can lead to erroneous end points when results such as shown in Figure 2.03 are evaluated.

Grunwald(26)described an objective method of end point detection for symmetrical conductometric and photometric titration curves which have no sharp change of slope. Grunwald's method first involves making a crude estimate of the end point from the experimental data. This estimate is corrected by successive approximations from selected points that are located on the curved part of the titration curve. These approximations are repeated until the successive estimates converge. Systematic experimental errors and errors due to deviations from Beer's Law are minimized. An end point precision of better than 0.5 percent is obtained. This method resembles that of Boulard, differing only in that the second point on the line following the end point is calculated. The formula for the calculation of this point has been developed only for the vicinity of the end point; a region where readings are least reliable. Further, the method assumes that the points are taken in the region of the end point. The method also requires that a large number of experimental points be obtained in this region.

J. Mika(27)employed a method of least mean squares. Although his procedure has a sound theoretical basis, it can be used only for regularly spaced points obtained by equal additions of titrant.

Litaneau and Cörmös(22)developed a method similar

to that of Mika based on the calculation of the point of intersection of two straight lines. The coefficients of the equations of the two lines (the ordinate and the angular coefficient) are determined by the method of least squares, independent of whether the titrant was added in equal volumes or not. In this way, the most probable straight lines are used, thus removing subjective factors which might affect the extrapolation method.

An extensive examination of the problems associated with the theory of amperometric precipitation titrations has been made by Khadeev(28,29). He considered the general titration reaction, $pA + qB \rightleftharpoons A_p B_q$ and pointed out that a prior knowledge of the slope of the titration curve at the end point enables this point to be calculated even when the two parts of the curve depart considerably from linearity.

Bazay(30)pointed out that although an amperometric end point can be calculated by a mathematically correct nongraphic method, the use of such a method may not be reliable, since it will be subject to considerable experimental error.

THEORETICAL SLOPE METHOD OF END POINT DETECTION

It is proposed that a technique for end point detection, called the theoretical slope method (T.S.M.), be used under conditions where there is strong curvature in the titration curves. This method has been proposed for titrations involving amperometric or photometric indicators. The method is rapid and precise and it has been generally applied to titration curves of the type illustrated in Figure 2.02. However, it is expected that under certain other instrumental conditions its use may be extended to other types of curves.

As was explained previously, the end points in Figures 2.02C, and 2.02D, can not be found accurately or precisely by the generally used extrapolation method of detection, due to the large amount of curvature. Figure 2.04 is a plot of three titration curves involving a metal indicator, for different ratios of conditional equilibrium constants $\left(\frac{K'_{MT^{+n}}}{K'_{IndT} + x}\right)$. In this figure, moles of unreacted indicator ion are plotted against moles of titrant added. In region 1 of this figure, M^{+n} is reacting primarily with the titrant added, $M^{+n} + T \rightleftharpoons MT^{+n}$, because of its larger conditional equilibrium constant. Region 2 corresponds to the part

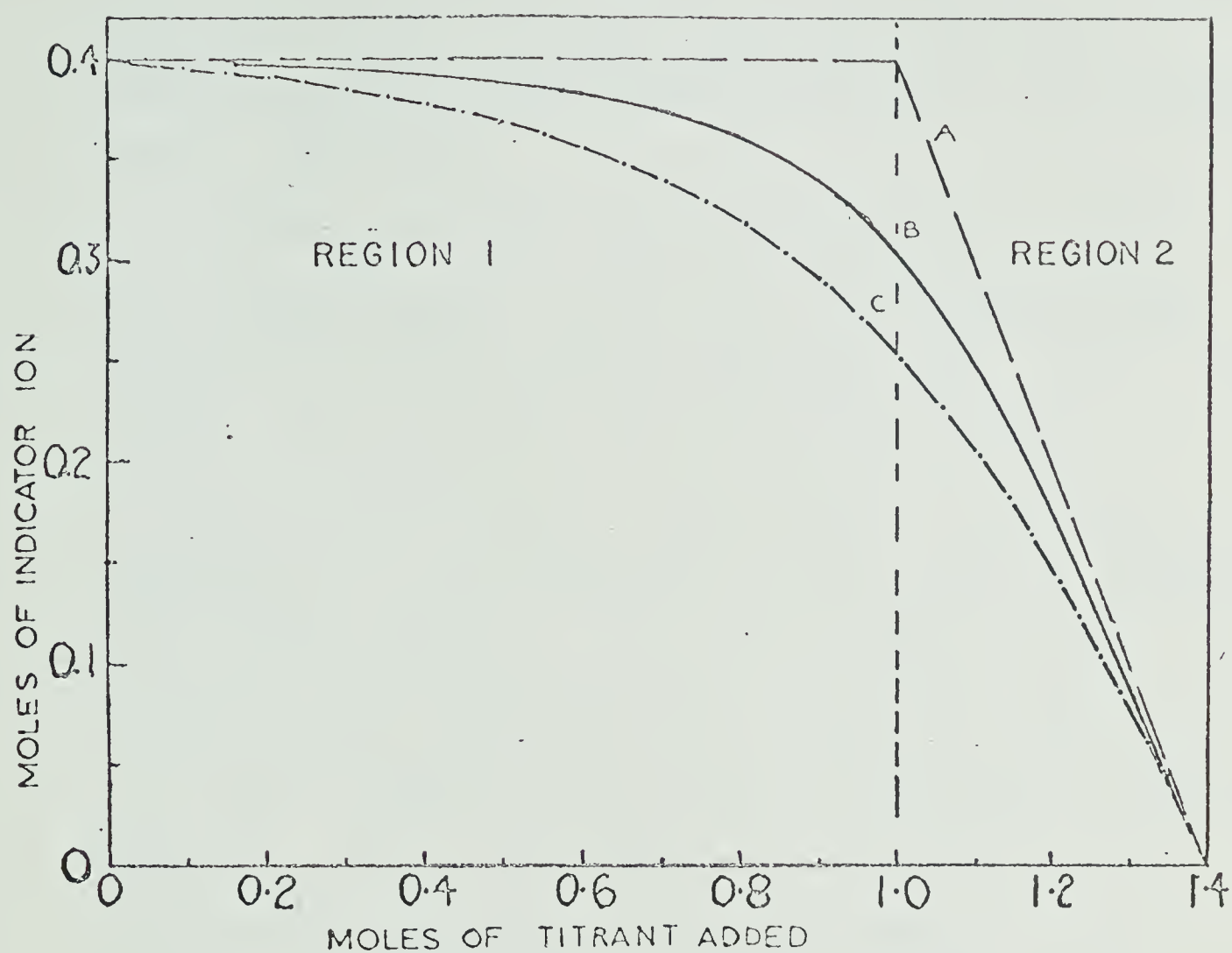


Figure 2.04 Curves for the titration of 1.0 moles of M^{+n} using 0.4 moles of Ind^{+x} as the indicator ion in coordinates of moles of indicator ion unreacted versus moles of titrant added. $K'_{MT} + n/K'_{IndT} + x$ has values of; A, 10^∞ ; B, $10^{1.5}$; C, $10^{1.0}$.

of the titration curve where M^{+n} has been predominately complexed and the indicator ion is now reacting to a larger extent with the titrant, according to the reaction, $\text{Ind}^{+x} + T \rightleftharpoons \text{IndT}^{+x}$.

Curve A in Figure 2.04 is an idealized titration curve ($K'_{MT}{}^{+n}/K'_{\text{IndT}}{}^{+x}$ is 10^∞) for a 1:1 stoichiometric reaction of titrant with the indicator ion. It is evident from the figure that the portion of the titration curve in region 1 has a slope of zero and an intercept of 0.4 corresponding to the amount of indicator ion initially present. It is also evident that the portion of the titration curve in region 2, from point (1.0, 0.4) to point (1.4, 0) has a slope that is equal to minus one. If the stoichiometry of the reaction of titrant with indicator ion was, for example, 1:2 or 1:3, the slope of the line in region 2 would be minus two or minus three. However, the slope of the line in region 1 will in all cases be zero and its intercept will correspond to the initial amount of indicator ion present.

Curves B and C in Figure 2.04 are titration curves in which $K'_{MT}{}^{+n}/K'_{\text{IndT}}{}^{+x}$ are $10^{1.5}$ and $10^{1.0}$. Both of these titration curves approach curve A at the extremes of the titration, that is, they approach straight lines which have a slope of zero in region 1 and a slope of minus one in region 2.

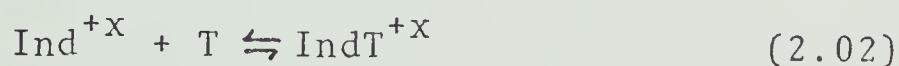
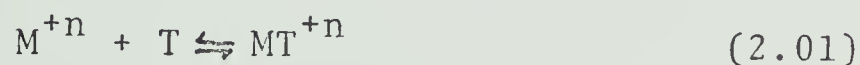
Experimentally it would be difficult to determine where curves B and C approach straight lines and

therefore when the extrapolation method of end point detection is applied to these curves, erroneous values would be obtained as will be shown in a following section. This difficulty could be reduced by knowing the position of one of the straight line portions. This is, in fact, known for the line in region 1. The extrapolated line in this region will theoretically have a slope of zero and an intercept corresponding to the known amount of indicator ion present when no titrant has been added. Unfortunately, knowledge of the position of the line in region 2 is not readily available when a large amount of curvature exists. If the value of the conditional equilibrium constant for the $\text{Ind}^{+x} + \text{T} \rightleftharpoons \text{IndT}^{+x}$ reaction is sufficiently large an accurate and precise end point is defined by a line in region 2 of slope minus one drawn through a point approaching 100% of the indicator ion reacted. It is, however, difficult to obtain consistently a particular point just short of 100% reaction of the indicator. Also, if the reaction between the titrant and the indicator ion is not complete then a point near 100% is poor because of the possible extent of curvature in that region.

The basis of the proposed theoretical slope method involves primarily the theory discussed above. If a point is chosen in region 2 that does not fall on the straight line portion and a line of slope minus one is

drawn through this point, meeting the line in region 1 of slope zero and intercept corresponding to amount of indicator ion present, then an end point of lower value than the equivalence point will be obtained. The T.S.M. allows correction of this experimental value. The correction factor is a function of the percent indicator ion reacted at the point chosen in region 2 and is also a function of the ratio of conditional equilibrium constants. This correction enables one to determine the end point accurately, regardless of the position of the point chosen in region 2. The obtaining and application of the correction factor is discussed in the following sections.

As mentioned above, the correction factor is dependent on a knowledge of the ratio of conditional equilibrium constants for the system under investigation. Schwarzenbach (31) carried out exhaustive determinations of conditional equilibrium constant ratios by polarographic means. Complexes with EGTA and EDTA were investigated. He was able to calculate the ratio of the constants by considering the reactions of the metal ions involved with the titrant. The general reactions are



The conditional equilibrium constants for reactions 2.01

and 2.02 are

$$K'_{MT^{+n}} = \frac{C_{MT^{+n}}}{C_{M^{+n}} \cdot C_T} ; \quad K'_{IndT^{+x}} = \frac{C_{IndT^{+x}}}{C_{Ind^{+x}} \cdot C_T} \quad (2.03)$$

and therefore

$$\frac{K'_{MT^{+n}}}{K'_{IndT^{+x}}} = \frac{C_{MT^{+n}} \cdot C_{Ind^{+x}}}{C_{IndT^{+x}} \cdot C_{M^{+n}}} \quad (2.04)$$

With a knowledge of the initial concentrations of Ind^{+x} and M^{+n} and measuring the concentration of Ind^{+x} after the addition of titrant, it is possible to calculate the ratio of the conditional equilibrium constants. In a less precise manner the ratio can be determined by fitting the experimental titration curve to a series of theoretical titration curves that are calculated for various ratios.

2.04 THE CORRECTION FACTOR IN THE THEORETICAL SLOPE METHOD

Equations 2.01, 2.02 and 2.03 are concerned with the reactions of the metal ion to be titrated and the indicator ion with the titrant.

It follows from these Equations that,

$$C_M^{+n} + C_{MT}^{+n} = C_1 \quad (2.05)$$

$$C_{Ind}^{+x} + C_{IndT}^{+x} = C_2 \quad (2.06)$$

$$C_{MT}^{+n} + C_{IndT}^{+x} + C_T = X \quad (2.07)$$

where C_1 is the concentration of M^{+n} initially present, C_2 is the concentration of Ind^{+x} initially present, C_M^{+n} is the total concentration of the metal ion not complexed with the titrant, C_{Ind}^{+x} is the total concentration of the indicator ion not complexed with titrant, C_T is the total concentration of uncomplexed titrant, C_{MT}^{+n} is the total concentration of metal ion complexed with titrant in the mole ratio of 1:1, C_{IndT}^{+x} is the total concentration of indicator ion complexed with titrant in the mole ratio of 1:1, and X is the concentration of titrant added.

From Equations 2.03 to 2.07 an equation of the form

$$\begin{aligned}
 & (K'_{\text{IndT}^{+x}} - K'_{\text{MT}^{+n}})C_{\text{Ind}^{+x}}^2 + (XK'_{\text{IndT}^{+x}} - C_T K'_{\text{IndT}^{+x}} \\
 & - C_2 K'_{\text{IndT}^{+x}} + C_1 K'_{\text{MT}^{+n}} - X K'_{\text{IndT}^{+x}} + C_T K'_{\text{MT}^{+n}} \\
 & + (C_2 K'_{\text{MT}^{+n}})^2)C_{\text{Ind}^{+x}} + X K'_{\text{MT}^{+n}} K'_{\text{IndT}^{+x}} - C_1 K'_{\text{MT}^{+n}} C_2 \\
 & - C_T K'_{\text{MT}^{+n}} C_2 - K'_{\text{MT}^{+n}} C_2 C_2 = 0
 \end{aligned} \tag{2.08}$$

can be obtained. Substitution of values of $K'_{\text{MT}^{+n}}$, $K'_{\text{IndT}^{+x}}$, C_2 and C_1 into this equation allows the calculation of $C_{\text{Ind}^{+x}}$, as a function of X , by making successive approximations of C_T . A computer program has been written that will perform this calculation and also allow the calculation of titration curves for various values of C_1 , C_2 , $K'_{\text{MT}^{+n}}$, and $K'_{\text{IndT}^{+x}}$. These calculations were performed on the University of Alberta I.B.M. 7040 Computer. The program used is shown in Figure 2.05. It contains instructions to calculate the end points that result when lines of slope minus one, passing through the calculated points in region 2, intersect a line in region 1 of slope zero and intercept equal to C_2 . In addition it calculates the percent end point error and contains instructions to plot the values of indicator ion unreacted against moles of titrant added.


```

1 100 READ(5,901)Q1,Q2,C1,C2,XMAX
2    IF(Q1.EQ.0.00)CALL EXIT
3 101 WRITE(6,910)Q1,Q2,C1,C2
4    WRITE(6,915)
5    CONST=+0.1000E-09
6    Q1=Q1*CONST
7    Q2=Q2*CONST
8    X=0.00
9    1 X=X+0.00001
10   T=0.00
11   S=0.00
12   IF (X.GT.XMAX) GO TO 105
13   2 T=S
14   A=Q2-Q1
15   B=X*Q2-T*Q2-C2*Q2+C1*Q1-X*Q1+T*Q1+C2*Q1+C2*Q1
16   C=X*Q1*C2-C1*Q1*C2-T*Q1*C2-Q1*C2*C2
17   IF(B*B.LT.4.0*A*C)GOTO102
18   D=SQRT(B*B-4.0*A*C)
19   O2=(-B+D)/(2.0*A)
20   O2T=C2-O2
21   O1T=X-T-O2T
22   O1=C1-O1T
23   IF (X.LT.C1 ) GO TO 3
24   IF (X.GE. C1 ) GO TO 4
25   3 S=O1T*CONST/((C1-O1T)*Q1)
26   GOTO5
27   4 S=O2T*CONST/((C2-O2T)*Q2)
28   5 IF(S-T.GT.0.000001E+00) GO TO 2
29   E=O2-C2+X
30   OK=((C1-E)/C1)*100.0
31   OKK=((C2-O2)/C2)*100.0
32   WRITE(6,920)X,O1,O2,E,OK,OKK
33   WRITE(3,920)X,OKK
34   GOTO1
35 102 WRITE(6,930)
36 105 WRITE(3,950)
37 GOTO100

```

Figure 2.05 Example of the program in Fortran language to calculate the titration curves for various ratios of conditional equilibrium constants and various concentrations of metal ion and indicator ion. The symbols used in this program are: Q_1 , conditional equilibrium constant for the more stable metal ion titrant (MT^{+n}) complex; Q_2 , conditional equilibrium constant for the less stable metal ion-titrant complex (indicator ion complex); X , concentration of the titrant in the reaction vessel; O_1 , concentration of M^{+n}

remaining after X has been added; 02, concentration of Ind^{+x} remaining after X has been added; 01T, concentration of MT^{+n} after X has been added; 02T, concentration of IndT^{+x} after X has been added; S, concentration of free titrant that exists in the reaction vessel after X has been added; E, end point found by the T.S.M.; OK, percent end point error; and OKK, percent of Ind^{+x} reacted after X has been added.

The Computer follows the instructions in the following order:

<u>Line Numbers</u>	<u>Meaning and Comments</u>
1.	Read the next set of data
2.	Exit when data card is blank
3.	Print the data
4.	Print headings for values to be calculated
5-7.	Adjust Q1 and Q2 to values that the computer can use
8-9.	Begin with calculation for X equal to 0.05
10-11.	Let concentration of free titrant be zero
12.	When X becomes equal to the concentrations of both ions, go to statement 10S
14-19.	Calculate the concentration of X that remains after $X = 0.05$ has been added
20.	Calculate the concentration of IndT^{+x}
21.	Calculate the concentration of MT^{+x}
22.	Calculate the concentration of M^{+n}
23-28.	Calculate the concentration of any free titrant that may be present and if it is significant go back to statement 2 and recalculate
29.	Calculate the end point by the T.S.M. method at the point where $X = 0.05$
30.	Calculate the percent end point error
31.	Calculate the percent of the indicator ion that has reacted
32.	Print out calculated data under appropriate headings
33.	Instruction for plotting by "Autoplotter"
34.	Go back to statement 1 and repeat the calculations for X equal to 0.10
37.	When X has become large enough go back to statement 100 and read next data card

A sample of the type of output obtained with this program is illustrated in Table 2.02 for a ratio of conditional equilibrium constants, $K'_{MT}{}^{+n}/K'_{Ind}{}^{+x}$, of 10 and for amounts of M^{+n} and Ind^{+x} in a mole ratio of 1.0 to 0.4.

TABLE 2.02 COMPUTER CALCULATED RESULTS FOR THE REACTION OF TITRANT WITH M^{+n} AND Ind^{+x} IN A MOLE RATIO OF 1.0 TO 0.4 AND WITH A VALUE OF $(K'_{MT}{}^{+n}/K'_{IndT}{}^{+x})$ of 100.

X	M1	M2	END PT	ERR	PER R
0.500000E-01	0.950209E 00	0.399779E 00	0.497905E-01	0.950209E 02	0.523701E-01
0.100000E 00	0.900442E 00	0.399558E 00	0.995582E-01	0.900442E 02	0.110446E 00
0.150000E 00	0.850701E 00	0.399299E 00	0.149299E 00	0.850701E 02	0.175195E 00
0.200000E 00	0.800991E 00	0.399009E 00	0.199009E 00	0.800991E 02	0.247837E 00
0.250000E 00	0.751320E 00	0.398680E 00	0.248680E 00	0.751320E 02	0.329900E 00
0.300000E 00	0.701613E 00	0.398307E 00	0.298307E 00	0.701693E 02	0.423326E 00
0.350000E 00	0.652172E 00	0.397878E 00	0.347878E 00	0.652122E 02	0.530623E 00
0.400000E 00	0.602620E 00	0.397380E 00	0.397380E 00	0.602620E 02	0.655097E 00
0.450000E 00	0.553205E 00	0.396795E 00	0.446795E 00	0.553205E 02	0.801179E 00
0.500000E 00	0.503900E 00	0.396100E 00	0.496100E 00	0.503900E 02	0.974923E 00
0.550000E 00	0.454739E 00	0.395261E 00	0.545261E 00	0.454739E 02	0.118485E 01
0.600000E 00	0.405773E 00	0.394227E 00	0.594227E 00	0.405773E 02	0.144329E 01
0.650000E 00	0.457075E 00	0.392925E 00	0.642925E 00	0.397075E 02	0.176868E 01
0.700000E 00	0.308759E 00	0.391241E 00	0.691241E 00	0.308759E 02	0.216975E 01
0.750000E 00	0.261013E 00	0.388987E 00	0.738987E 00	0.261013E 02	0.275327E 01
0.800000E 00	0.214158E 00	0.385842E 00	0.785842E 00	0.214158E 02	0.353956E 01
0.850000E 00	0.168775E 00	0.381225E 00	0.831225E 00	0.168775E 02	0.469386E 01
0.900000E 00	0.125956E 00	0.374044E 00	0.874044E 00	0.125956E 02	0.648899E 01
0.950000E 00	0.876926E-01	0.362307E 00	0.912307E 00	0.876926E 01	0.942313E 01
0.100000E 01	0.568855E-01	0.343115E 00	0.943114E 00	0.568855E 01	0.142214E 02
0.105000E 01	0.354858E-01	0.314514E 00	0.964514E 00	0.354858E 01	0.213714E 02
0.110000E 01	0.222222E-01	0.277778E 00	0.977778E 00	0.222222E 01	0.305555E 02
0.115000E 01	0.141626E-01	0.235837E 00	0.985837E 00	0.141626E 01	0.410406E 02
0.120000E 01	0.905138E-02	0.190949E 00	0.990949E 00	0.905138E 00	0.522628E 02
0.125000E 01	0.561671E-02	0.144383E 00	0.994383E 00	0.561671E 00	0.539042E 02
0.130000E 01	0.318319E-02	0.968169E-01	0.996817E 00	0.318319E 00	0.757958E 02
0.135000E 01	0.138171E-02	0.486184E-01	0.998618E 00	0.138171E 00	0.878454E 02

The computer is instructed to determine various end points by finding the intersection of a line in region 1, of slope zero and an intercept corresponding to the initial concentration of indicator ion, with lines through various points in region 2 of slope minus one. The coordinates for each point are the numbers given in columns 1 and 3 of Table 2.02. The end points found for each point are given in column 4. The end point error (column 5) was found by subtracting

the value found in column 4 from the initial amount of M^{+n} , i.e., 1.0 and then multiplying by 100/1.0. Column 6 is the percent of the indicator ion reacted after each addition of titrant. A plot of values such as given in columns 5 and 6 of percent end point error versus percent indicator ion reacted is shown in Figure 2.06 for different values of the ratio of the conditional equilibrium constant for MT^{+n} to the conditional equilibrium constant for $IndT^{+x}$. It is from a figure such as this that the correction factor is obtained.

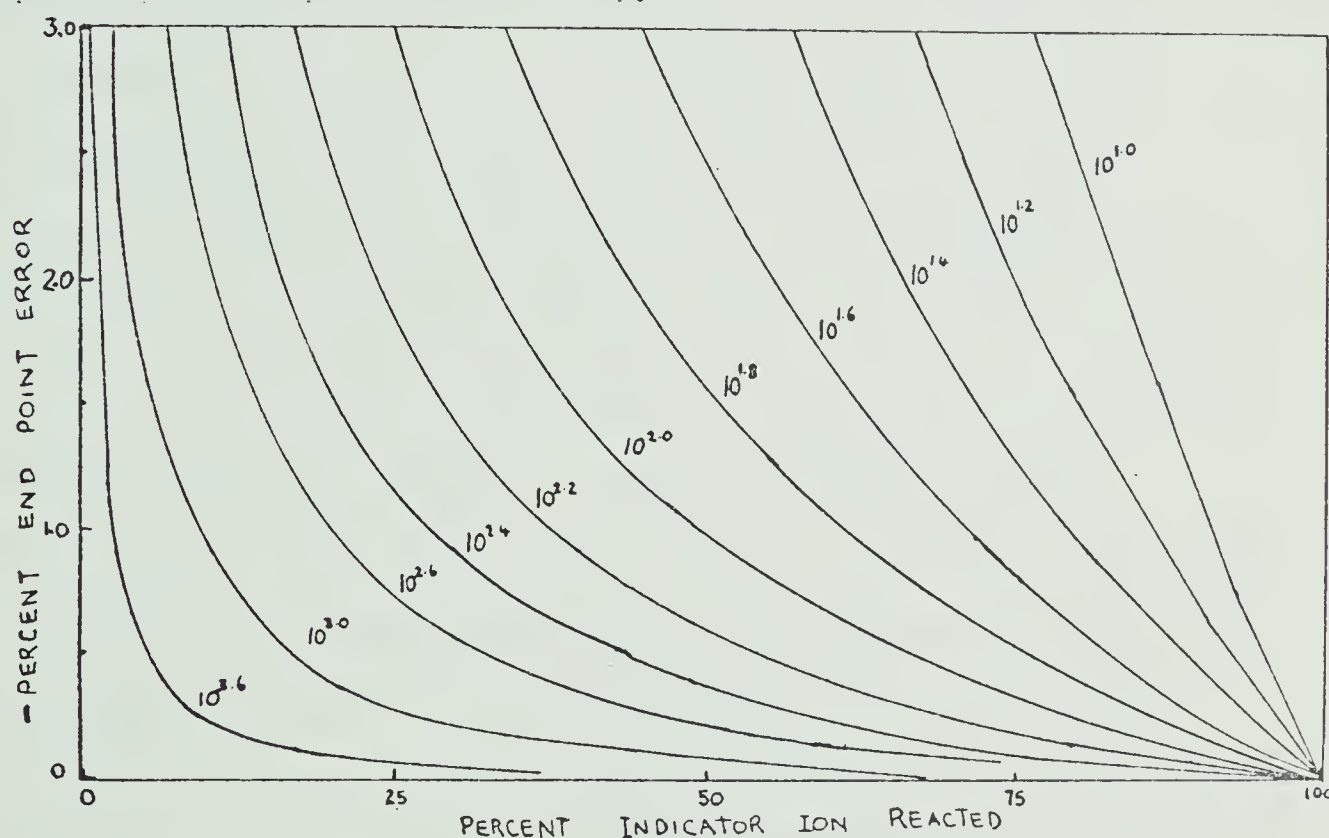


Figure 2.06 Correction graph for the application of the theoretical slope method of end point detection. Each line corresponds to a different value of $K'_{MT^{+n}}/K'_{Ind^{+x}}$.

Each curve in Figure 2.06 was found to be independent of the ratio of the initial concentration of the sought after ion to the initial concentration of the indicator ion ($[M^{+n}]/[Ind^{+x}]$). Each curve has a maximum ordinate value of 100 at zero percent of the indicator reacted and a

minimum ordinate value of zero at 100% of the indicator reacted. The ordinate value in the region of 90 to 100% indicator ion reacted will, however, be larger if the equilibrium constant for the $\text{Ind}^{+x} + \text{T} \rightleftharpoons \text{IndT}^{+x}$ reaction is small.

The shapes of the curves in Figure 2.06 are such that for large ratios of the conditional equilibrium constants the T.S.M. will generally give small end point errors for all points in region 2 (defined in Figure 2.04) ranging from a small amount of indicator ion reacted to nearly complete reaction of the indicator. For points corresponding to a smaller percent of the indicator reacted, the end point error is too large to apply a correction with validity. For example for a conditional equilibrium constant ratio of $10^{2.6}$, a large end point error will be obtained if the T.S.M. is applied using the point in region 2 corresponding to about 5 percent of the indicator ion reacted. A smaller end point error will be obtained, however, if a point corresponding to a greater amount of indicator ion reacted is chosen.

As the ratio of the conditional equilibrium constants decreases, it becomes more and more important to obtain readings corresponding to more nearly complete reaction of the indicator ion. For example, with a ratio of $10^{3.0}$ the error is unacceptably large at 5 percent of the indicator reacted, whereas at 25 percent it is small and at still higher percent reacted it is negligible. On the other hand with a ratio of $10^{2.0}$ the error at 25 percent

of the indicator reacted is too large and a reading at 50 percent reacted or greater is required. In a still more extreme example, for a conditional equilibrium constant ratio of 1.0, the end point error is unacceptably large at about 80 percent indicator ion reacted, and a reading corresponding to more indicator reacted is required. At 95 percent reacted an end point error of -0.5 percent is still obtained.

As described above, if the ratio of conditional equilibrium constants is not large, then a correction may be needed to obtain a valid end point. To obtain this correction the approximate value of the ratio must be known and the point in region 2 should be chosen that will not require an excessively large correction. The uncorrected end point is calculated according to the formula:

$$\begin{aligned} \text{UNCORRECTED END POINT} &= \text{MOLES OF TITRANT ADDED} - \\ &\quad \text{INITIAL MOLES OF INDICATOR ION} + \\ &\quad \text{MOLES OF INDICATOR ION UNREACTED} \end{aligned} \quad (2.09)$$

It should be pointed out that this formula applies only to a 1:1 stoichiometry between the indicator ion and the titrant. For a different ratio, the formula would have to be correspondingly modified.

The end point is then corrected by obtaining a correction value from Figure 2.06 (if the stoichiometry

is 1:1). As explained above, for large ratios of conditional equilibrium constants, the point in region 2 can be chosen with considerable freedom. If the ratio is large enough the uncorrected end point is not significantly different from the correct value and no correction need be applied. For this reason the ratio need not be known precisely. If the ratio is moderately large, then a small correction may need to be applied. For small ratios the end point error will be large at points corresponding to low percentages of indicator reacted and the correction must be applied in these cases. To obtain the correction requires both a knowledge of the ratio of the conditional equilibrium constants and readings at large percentages of the indicator reacted. The next section describes how to obtain and apply such corrections.

2.05 RECOMMENDED PROCEDURE FOR THE USE OF THE THEORETICAL SLOPE METHOD

The theoretical slope method is primarily recommended for the titration systems involving a metal ion indicator that give titration curves of the type illustrated in Figure 2.04. It requires that the ratio of the conditional equilibrium constants for the system be determined or known initially. However, depending on the accuracy required, the ratio need not be known if the ratio exceeds 10^2 as Figure 2.06 shows. For its successful application, the method requires that only three measurements be made at selected places on the titration curve; initially, i.e., before any titrant has been added; when 85 to 100 percent of the indicator ion has reacted; and finally when the indicator ion has completely reacted. The T.S.M. is of specific use when the ratio of the conditional equilibrium constants is less than 10^2 and the extrapolation method is invalid. While the method has been specifically developed and is recommended for systems with a conditional equilibrium constant ratio of less than 10^2 its use is not restricted to such systems. In reality the T.S.M. may even be considered to be advantageous for systems with larger ratios, especially where a large number of titrations must be routinely carried out, because only a few measurements need be made.

GENERAL PROCEDURE

A - Test of suitability of an indicator ion.

Choose an indicator ion that forms a less stable complex with the titrant than does the metal ion to be titrated. In the case of an amperometric titration, add an aliquot of a standard solution of the metal ion to be determined to the titration vessel. Adjust the pH to the desired value by the addition of buffer. Adjust the ionic strength to about 0.1. Dilute to 50 mls. Determine its current voltage curve (if any) versus a saturated calomel reference electrode using a D.M.E. or R.P.E. indicator electrode.

To another titration vessel add an aliquot of standard indicator ion solution. Adjust the pH and ionic strength to the same values as above. Dilute to 50 mls. Determine its current voltage curve using the same indicator and reference electrodes as above. Add an aliquot of standard titrant. Measure the current voltage curve again. Continue to add titrant and measure the current voltage curves until the diffusion current does not change upon addition of more titrant. Correct each curve for dilution effects. Make a plot of diffusion current, at a potential on the diffusion plateau, versus volume of titrant added. A straight line should be obtained which intersects the base line at a point

corresponding to the stoichiometry of the reaction.

In a similar manner, double check that the current voltage curve for a solution containing the above amounts of indicator ion and metal ion to be titrated under the above conditions of pH and ionic strength is the same as that obtained for the indicator ion reduction in the absence of the metal ion to be titrated.

In the case of a photometric indicator the same general procedure should be followed to make certain that the indicator ion is the only substance that absorbs light at a particular wavelength. Interference at that wavelength by any of the reactants or products of the reactions may necessitate choice of a different indicator. As with the amperometric indicator, it will be necessary to determine the stoichiometry of the indicator ion and titrant reaction.

B - Determination of the ratio of
conditional equilibrium constants.

Add 10 ml. portions of a standard solution of the metal ion to be titrated to six 50 ml volumetric flasks. Add 10 mls of a standard solution of indicator ion to each flask and adjust the pH to a value appropriate for the titration reaction. Adjust the ionic strength so that it will have the same final value in each flask. Dilute one of the flasks to volume with deionized water. To the remaining five successive flasks add $1/5$, $2/5$, $3/5$, $4/5$, and $6/5$ of the amount of titrant required to react completely with both the metal and indicator ions. Dilute the flasks to volume. Adjust the potential versus S.C.E. or wavelength to the desired value. Measure the diffusion currents or absorbances for the indicator ion in each of the flasks at the same and constant temperature. Calculate the ratio of the conditional equilibrium constants in the manner previously described (Section 2.03, page 39).

C - The Titration

Introduce an aliquot of the metal ion solution of unknown concentration into the titration vessel. Pipet an aliquot of standard indicator ion solution, in an amount approximately equal to the metal ion added. Adjust the pH to the same value at which the conditional equilibrium constant ratio was determined. Adjust the

ionic strength also to the same value used for the ratio determination. Dilute to approximately 50 mls. Set the potential or wavelength at the desired value. Record the initial reading of diffusion current in the case of an amperometric titration or absorbance in the case of a photometric titration. Add an amount of standard titrant from a calibrated buret so that the concentration of the indicator ion corresponds to between 85 and 95 percent reacted. Measure the diffusion current or absorbance. Add an amount of titrant in excess of the amount needed to react completely with the metal ion and the indicator ion. Measure the residual current or absorbance reading. Subtract the residual current or absorbance reading from the two others and correct for dilution if necessary. During these measurements the solution should be at room temperature or in any case it should not be allowed to vary.

Convert the readings into moles of indicator ion unreacted and also into units of percent indicator ion reacted. Convert the volume of titrant added into moles of titrant added.

The percent indicator ion reacted may be calculated from the formula,

$$\begin{aligned} \text{PERCENT OF INDICATOR} &= \frac{V_I M_I - \left(\frac{B}{A}\right) V_I M_I}{V_I M_I} \cdot 100 \\ \text{ION REACTED} & \\ &= 100 - \left(\frac{B}{A}\right) 100 \end{aligned} \quad (2.10)$$

where V_I is the volume of the aliquot of standard indicator ion solution added in liters; M_I is the molarity of the standard indicator ion solution; A is the current or absorbance reading for the initial point; B is the current or absorbance reading at the point of 85 to 95% of the indicator ion reacted.

From percent reaction value read the percent correction to be applied (CORR), from Figure 2.06.

Calculate the end point from the following formula:

$$\begin{aligned} \text{END POINT (moles)} &= V_T M_T - V_I M_I + \left(\frac{B}{A}\right) V_I M_I \\ &+ \text{CORRECTION} \end{aligned} \quad (2.11)$$

where,

$$\text{CORRECTION} = [V_T M_T - V_I M_I + \left(\frac{B}{A}\right) V_I M_I] \cdot \frac{\text{CORR}}{100} \quad (2.12)$$

V_T is the volume in liters of the titrant added at the current or absorbance reading, B and M_T is the molarity of the titrant.

3. STATISTICAL RESULTS

In this chapter the extrapolation method of finding end points in titrations involving metal indicator ions is examined in greater detail, particularly from an experimental point of view. Statistical data was collected in an attempt to evaluate the effects of the angle between the extrapolated lines, the amount of extrapolation needed and the ratio of the conditional equilibrium constants on the precision and accuracy of end points found by this method. Finally, the effect of the ratio of conditional equilibrium constants on the accuracy of the extrapolation method is compared with its effect on the accuracy of the theoretical slope method.

3.01 - STATISTICAL INVESTIGATION OF FACTORS THAT INFLUENCE THE PRECISION OF THE EXTRAPOLATION METHOD OF END POINT DETECTION

A study was carried out to statistically determine the effect of certain factors on the precision of the end point found by the extrapolation procedure. The factors investigated were: the angle (α) made by the two extrapolated lines, the portions (ϕ) of the extrapolated lines that are established by points and finally the effect of the separation (Δ) of these points. The data were obtained with the aid of analytical chemistry students. They were asked to carry out the instructions given in Figure 3.01.

This exercise was given in conjunction with a laboratory experiment dealing with a photometric titration of Fe^{+3} using EDTA as the titrant and salicylic acid as the photometric indicator. Written instructions were also given on the technique of measuring the distance between two lines. Included in these instructions was also the technique of interpolating the distances between lines on a ruler. The rulers that were used in this project had fine lines that occupy only ten percent of the smallest interval. The students were instructed to use this line width to aid in the interpolation of the nearest hundredth's digit. In addition to being aware of the width of the scale lines, they were also made aware of the usefulness of working consistently from the line edges. Edges of the lines are precisely defined whereas line centers are not.

Figure 3.02 illustrates the technique that was recommended.

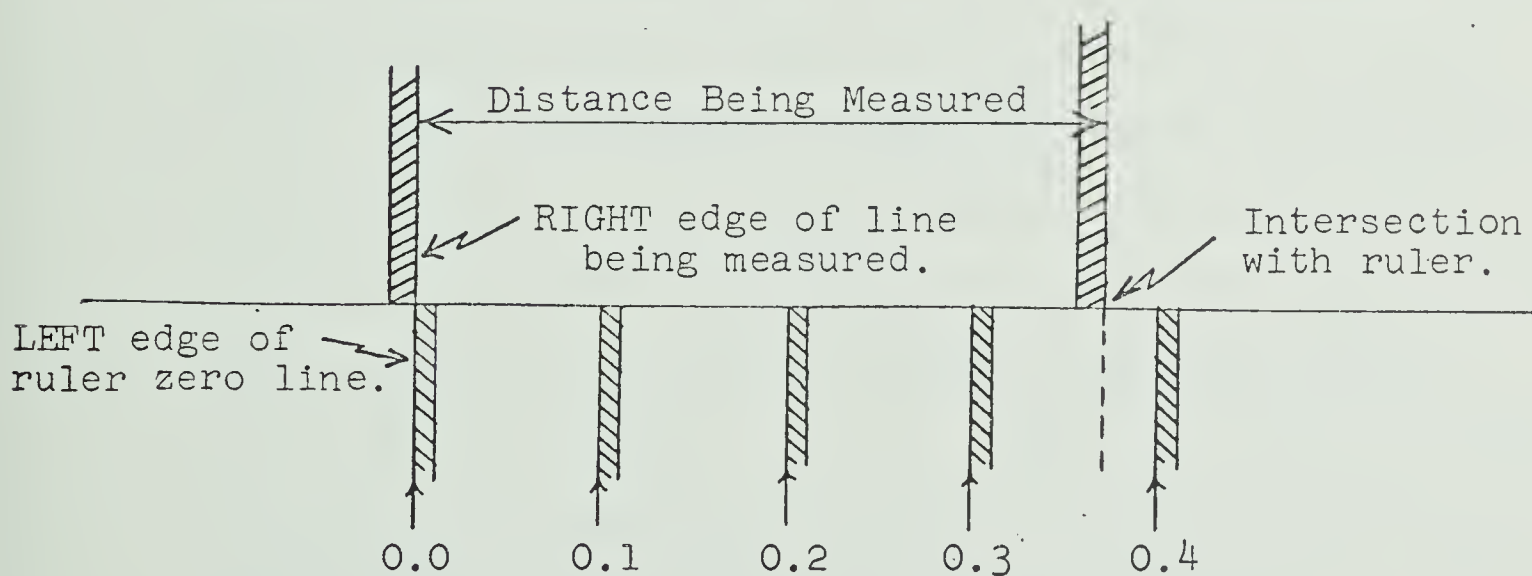


Figure 3.02 Example of measurement technique. In this example the reading is 0.37.

In all parts of Figure 3.01, the horizontal line corresponding to the extrapolated line in region 1 of Figure 2.04 was already supplied so that part of the extrapolation procedure was not required. The end point precision observed is thus due to the influence of variable factors in region 2 (Figure 2.04).

Part C in Figure 3.01 was designed to investigate the effect of the acute angle (α) between the horizontal line in region 1 and the extrapolated line in region 2. All sections of part C were provided with a large number of points to minimize presumed effects on precision due to factors such as the length of the line in region 2 defined by points.

Ball, Harris and Habgood (32) developed an equation for the reading error arising from the measurement of distances between two straight lines as a function of the angle between these lines. A modified form of their equation can be derived using their basic assumptions. The relationship between the error and the angle can be derived by considering Figure 3.03 A and 3.03 B. A minimum value of the reading error would be expected when measuring the distance between two well defined parallel lines (Figure 3.03 A). The error would increase to infinity as the angle between the ruler and the right line decreases from 90° to 0° (Figure 3.03 B).

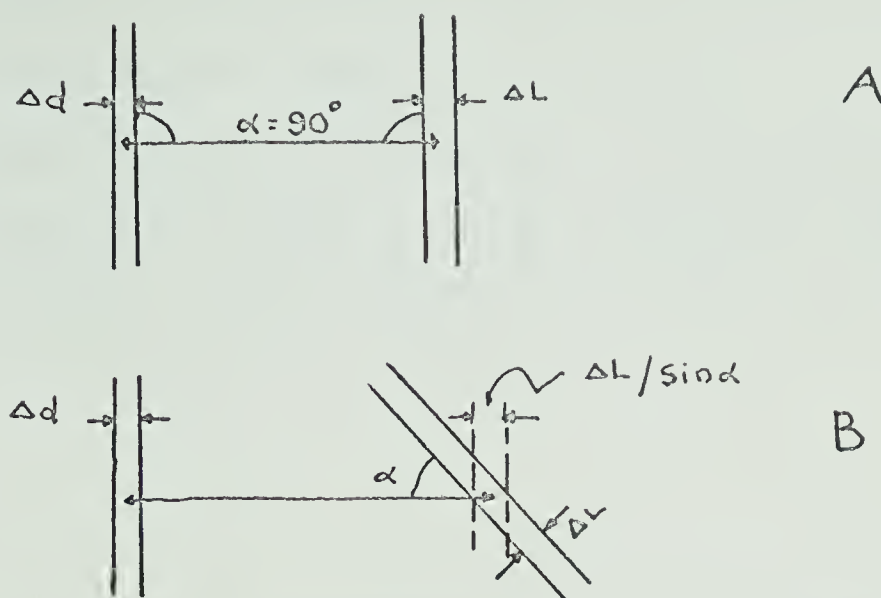


Figure 3.03 Schematic representation of factors contributing to reading error.

A, between parallel lines, ΔM_α is $\sqrt{\Delta d^2 + \Delta L^2}$;

B, between two lines when one line is sloping, the expected ΔM_α is

$\sqrt{\Delta d^2(\text{left side of figure}) + (\Delta L/\sin \alpha)^2(\text{right side of figure})}$.

Assume the left line of Figure 3.03 A to have a band of uncertainty of width Δd , and the right side to have a band of uncertainty of width ΔL . The uncertainty of a measurement, ΔM_α , between two lines, one of which forms an angle, α , with the ruler might then be expected to be,

$$\Delta M_\alpha = \sqrt{\Delta d^2 + \left(\frac{\Delta L}{\sin \alpha}\right)^2} \quad (3.01)$$

or the equivalent expression,

$$\Delta M_\alpha = \sqrt{\Delta d^2 + [\Delta L(1 + \cot^2 \alpha)]^2} \quad (3.02)$$

From the data of Ball and coworkers a value of Δd of 0.006 cm seems reasonable for this particular group of observers. In their work Δd would be equal to ΔL . In this investigation only one line is fixed and the sloping line is drawn experimentally. It is therefore

expected that ΔL will not be equal to Δd and in fact ΔL must generally be larger.

When the effect of the angle, α , on the standard deviation was investigated at four different angles, the statistical results obtained are shown in Table 3.01.

TABLE 3.01 RESULTS OF STATISTICAL INVESTIGATION OF THE EFFECT OF THE ANGLE BETWEEN THE EXTRAPOLATED LINES ON THE PRECISION WITH WHICH THE INTERSECTION CAN BE READ.

Angle of Intersection, Degrees	Average Value of Intersection, cm.	Standard Deviation, ΔM_{α}^*
37	5.223	0.031
54	8.847	0.029
68	11.498	0.025
83	15.119	0.022

* Each of these values is the result of about 60 independent measurements.

Figure 3.04 shows that the derived relationship between the angle, α , and the precision, given by Equations 3.01 and 3.02 is not inconsistent with the experimental results.

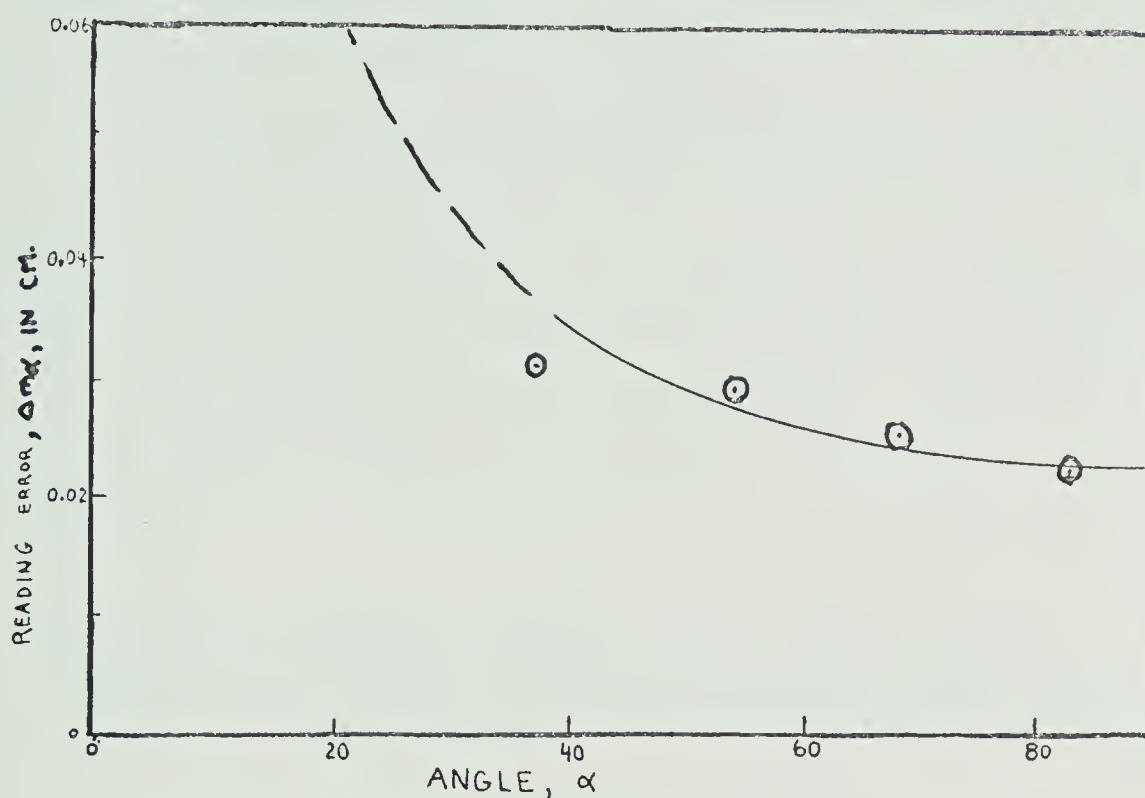


Figure 3.04 Dependence of reading error, ΔM_α , on the angle between the extrapolated lines. @, Experimental points; line is calculated from Equation 3.01 for Δm_α at 90° of 0.0225.

The results indicate that as the angle between the extrapolated lines approaches 90 degrees; the precision of the end point reading will reach its best value. This is consistent with the results obtained by Ball and coworkers. Figure 3.04 suggests that when the angle is much less than about 30° , the precision of the measurements can be expected to deteriorate seriously. If a value of Δd of 0.006, and the value of ΔM_α at 90° in Figure 3.04 is substituted in Equation 3.01 a value of

0.022 is obtained for ΔL . The error Δd therefore makes a negligible contribution to the overall error, and the more important source of error, ΔL , is associated with drawing of the line in Region 2.

Part A of Figure 3.01 was designed to investigate the effect of the length of the segment of the line in region 2 that is available for extrapolation purposes (ϕ), on the band of uncertainty, ΔL and thus the effect on the precision of the measurement. The symbol, ϕ , is defined by,

$$\phi = \frac{\text{Distance between 1st and last points used}}{\text{Length of extrapolated plus interpolated lines}} \times 100 \quad (3.03)$$

For example, in section IV of Figure 3.01 A, ϕ is equal to $\frac{\text{distance from 0 to } u}{\text{distance from point of intersection to } u} \times 100$.

To minimize the effect on the precision of the acute angle between the two lines, the value of the angle was 76° in all sections of Figure 3.01A.

The experimental results obtained for Figure 3.01A are shown in Table 3.02 and illustrated in Figure 3.05. Figure 3.05 indicates that as the portion of the line in region 2 becomes less well defined by points, the precision with which the end point can be measured probably becomes less. It is to be expected that the best precision is obtained when little or no extrapolation is required, i.e., when ϕ is greater than about 70 percent.

TABLE 3.02 RESULTS OF THE STATISTICAL INVESTIGATION OF THE EFFECT OF ϕ ON THE PRECISION OF THE EXTRAPOLATION PROCEDURE WHEN THE ACUTE ANGLE BETWEEN THE LINES IS 76° .

ϕ	Average value of the Intersection, cm.*	Standard Deviation, ΔM_α^*
31	3.139	0.028
62	6.974	0.024
78	9.895	0.019
81	<u> </u>	0.023**
93	11.276	0.022

* Each of these values are the result of about 60 independent measurements.

** This is a value obtained from Figure 3.04 for an α value of 76° .

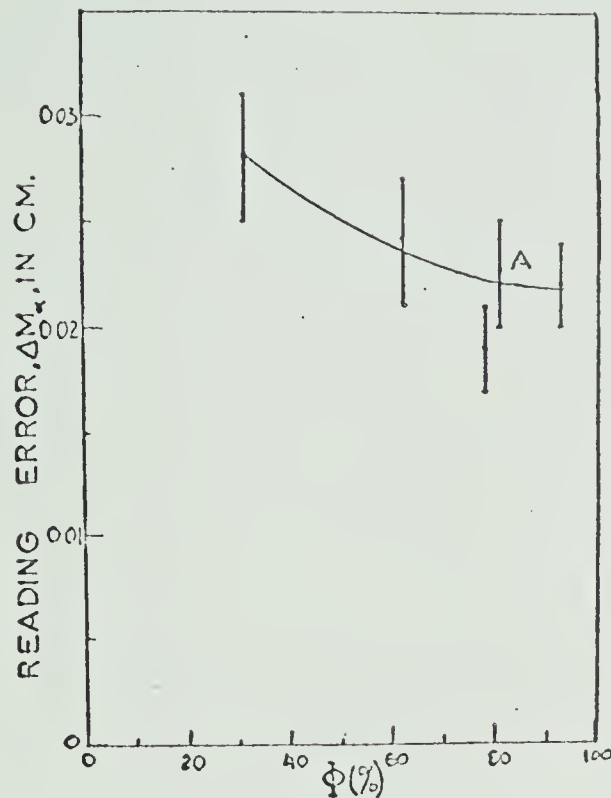


Figure 3.05 Dependence of reading error, ΔM_α , on the length of the segment of the line in region 2 that is available for extrapolation purposes. α is 76° . Point A is the value of ΔM_α obtained from figure 3.04.

An explanation of the expectation that better precision can be obtained when little or no extrapolation is required can be seen from a consideration of Figure 3.03. When the data of Table 3.02 along with a value of Δd of 0.006 is substituted into Equation 3.01, then values of ΔL as a function of ϕ are obtained, as shown in Figure 3.06. As is expected and as Figure 3.06 would suggest, a large band of uncertainty, ΔL , would result when extrapolating from a longer distance.

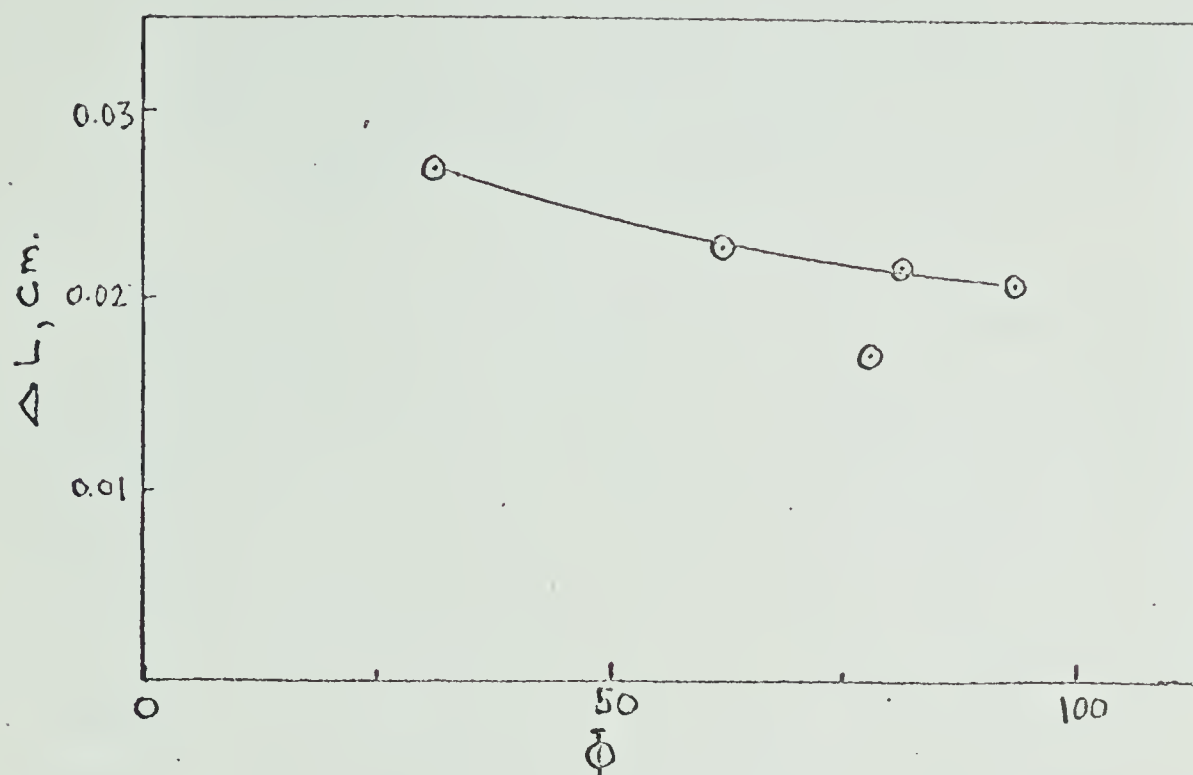


Figure 3.06 Dependence of ΔL on the length of the segment of the line in region 2 that is available for extrapolation purposes.

Investigation into the possible effect of the separation of the points on the value of ΔL , gave values of ΔM_α that were not statistically different. This suggests that for the successful application of the extrapolation method of end point detection a large number of points is not required. The requirement is that the points obtained appear on as much of the straight line portion as possible; that is, Φ should be large.

3.02 - STATISTICAL INVESTIGATION OF THE EFFECT OF THE RATIO OF THE CONDITIONAL EQUILIBRIUM CONSTANTS ON THE PRECISION AND ACCURACY OF THE EXTRAPOLATION METHOD OF END POINT DETECTION.

Experimental evaluation of the effect of the ratio of the conditional equilibrium constants on the precision and accuracy of the extrapolation method of end point detection was obtained by using the services of several graduate students in chemistry. The students were randomly divided into two groups. Each group was given computer calculated titration curves shown in Figure 3.07 and general instructions on the measurement

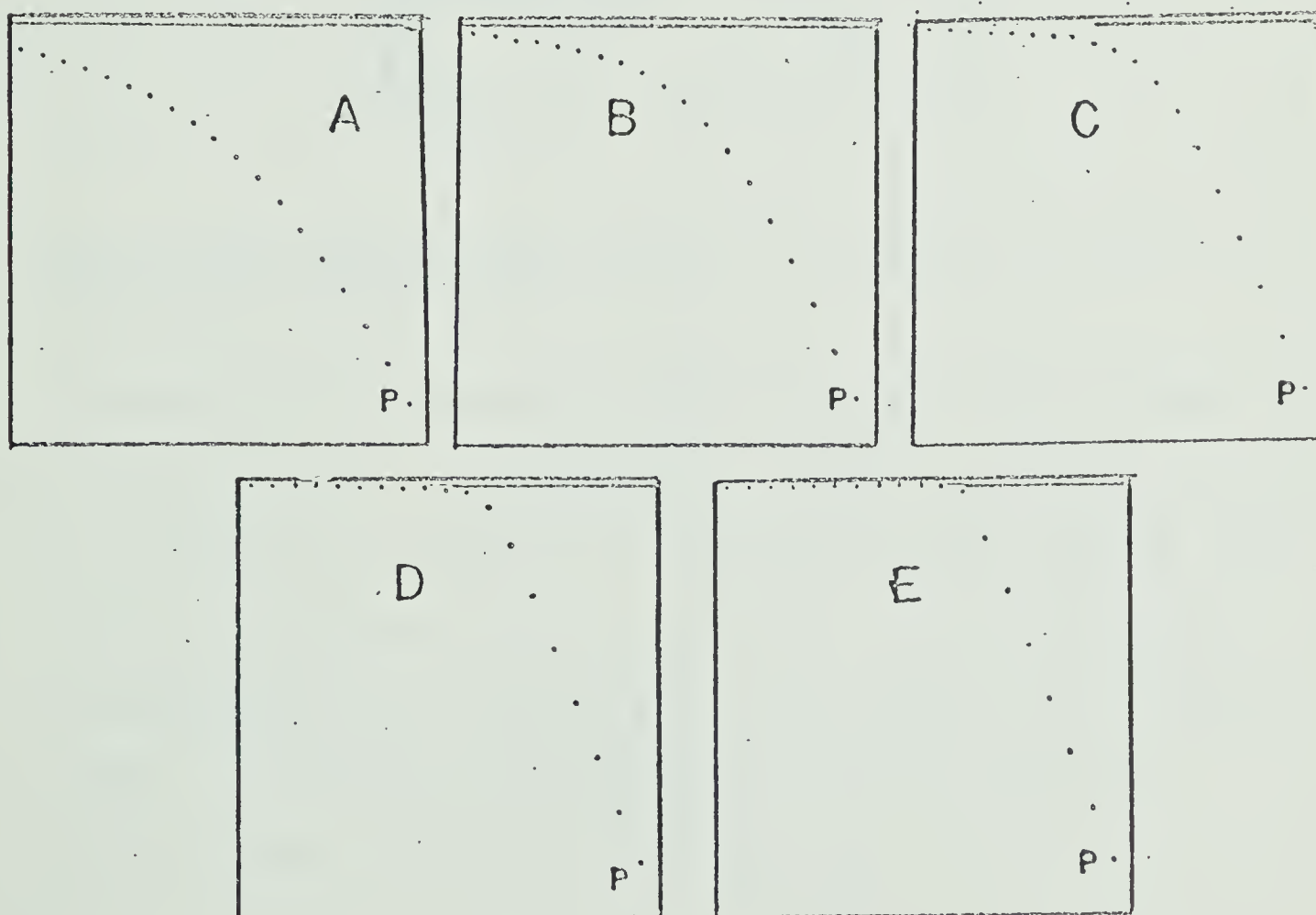


Figure 3.07 Computer calculated points used for the statistical investigation of the effect of the ratio of the conditional equilibrium constants on the precision and accuracy of the extrapolation method of end point detection. The ratios are; A, $10^{1.0}$; B, $10^{1.5}$; C, $10^{2.0}$; D, $10^{3.0}$; E, $10^{4.0}$.

techniques. One group was asked to draw a straight line through the center of point P, on each curve, and the center of as many consecutive points as possible. They were instructed to extend the line to the top of the graph, intersecting the horizontal line which was drawn in. This horizontal line corresponds to the line in region 1 of Figure 2.04 and the extrapolated line corresponds to the line in region 2 of that figure. They were then instructed to measure the distance indicated in Figure 3.08. The

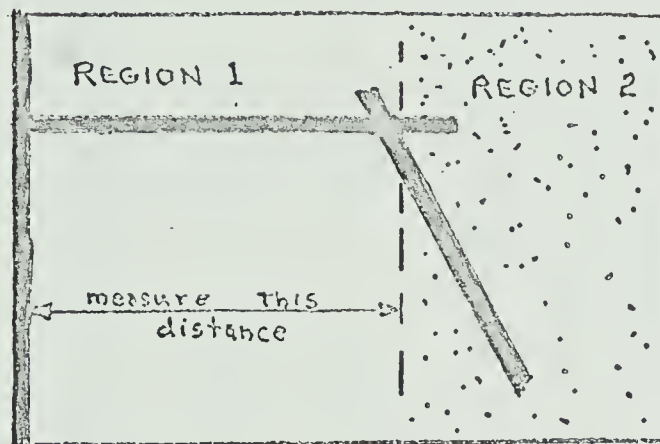


Figure 3.08 Schematic representation of the distance to be measured on each part of Figure 3.07.

second group was asked to draw a straight line through the center of point P and touching as many consecutive points as possible, in contrast to drawing the line through the center of as many points as possible. The remaining instructions were identical to those given to the first group. The reason for having each line in region 2 drawn through the center of point P was to have at

TABLE 3.03 RESULTS OF END POINT DETECTION BY THE TWO EXTRAPOLATION PROCEDURES

log K' MT ⁺ⁿ /K' IndT ^{+x}	Results for First Group				
	1.0	1.5	2.0	3.0	4.0
Average Measurement (cm)*	11.05	13.34	14.23	14.55	14.65
Average End Point (Fraction of theoretical end point)	0.858***	0.949	0.984	0.994	0.998
Standard Deviation (cm)*	0.07	0.10	0.03	0.03	0.03
Absolute End Point Error (%)	-14.2	-5.12	-1.61	-0.55	-0.16

log K' MT ⁺ⁿ /K' IndT ^{+x}	Results for Second Group				
	1.0	1.5	2.0	3.0	4.0
Average Measurement (cm)**	10.87	13.18	14.13	14.53	14.63
Average End Point (Fraction of theoretical end point)	0.850	0.942	0.980	0.994	0.998
Standard Deviation (cm)**	0.15	0.10	0.12	0.04	0.04
Absolute End Point Error (%)	-15.0	-5.75	-2.01	-0.63	-0.24

* Each of these values are the result of about 25 independent measurements.

** Each of these values are the result of about 50 independent measurements.

*** Figures 3.07A to E do not include all the points in region 1 of the titration curves. the distance from T equal to zero to the true end point is 25.40 cm. Independent measurements found the distance to the true end point from the right edge of the left hand line to be 14.67 cm. for graph A and 14.64, 14.65, 14.70 and 14.69 cm. for graphs B, C, D, and E. When these values are subtracted from 25.40 cm.; the distances to the right edge of the left hand line from T equal to zero are obtained. For example, for graph A (first group) the distance to the right edge of the left hand line from T equal to zero would be 10.73 cm (25.40 - 14.67). This value is added to the average measurement of 11.05 cm. and a value of 21.78 is obtained. This value indicates an end point (in fraction of theoretical end point) of 0.858 for Figure 3.07 A when the first extrapolation method is applied.

least one point common to every measurement. Point P on Figures 3.07A to 3.07E were all within 3 percent of each other and the initial amounts of metal ion to be determined and the indicator ion were in a mole ratio of 1.0 to 0.4.

The results for the two groups are shown in Table 3.03. The table shows that better precision and lower end point errors were obtained by the first group. For example the standard deviation for the first group was 0.07 cm for Figure 3.07A whereas the standard deviation for the second group was 0.15 cm. The results for both groups indicate also, that in general the standard deviation decreases as the ratio of the conditional equilibrium constants increases. Table 3.04 shows the results of applying the T.S.M. to the determination of the end points for the curves that were evaluated by the two groups described above.

The values of the uncorrected end points in the fourth row of Table 3.04 were obtained by applying the T.S.M. to the points in region 2 corresponding to the percent of indicator reacted given in row three. As was expected, the error in the uncorrected end point becomes smaller as the ratio of the conditional equilibrium constants becomes larger. The absolute standard deviation of 0.08 given in row five is the same for each ratio of conditional equilibrium constants and was estimated by considering factors illustrated in Figure 3.09.

TABLE 3.04 RESULTS OF END POINT DETECTION BY THE THEORETICAL
SLOPE METHOD

GRAPH	A	B	C	D	E
$\log \frac{K'_{MT^{+n}}}{K'_{IndT^{+x}}}$	1.0	1.5	2.0	3.0	4.0
Percent Indicator Reacted	90.2	88.5	87.8	87.5	87.5
Uncorrected End Point (fraction of theoretical end point)	0.989	0.996	0.999	1.00	1.00
Standard Deviation (cm)*	0.08	0.08	0.08	0.08	0.08
% Uncorrected End Point Error	1.1	0.4	0.1	negligible	

* Out of about 145 cm (see Table 3.03).

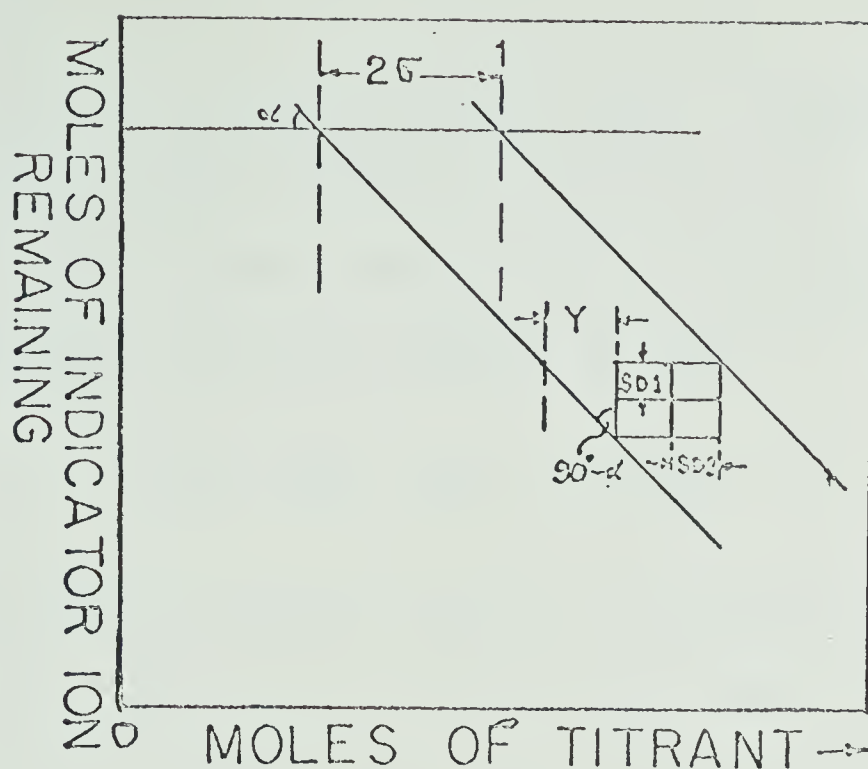


Figure 3.09 Schematic representation of the precision of one end point determination by the theoretical slope method.

Figure 3.09 has been drawn on the assumption that any point in region 2 has standard deviations in the x and y directions, as shown schematically. SD_1 is the standard deviation in the y direction and SD_2 is the standard deviation in the x direction. σ is the maximum end point standard deviation that can be expected to be found by the T.S.M. Y is equal to $2\sigma - 2 SD_2$. Therefore,

$$2\sigma = 2 SD_2 + Y \quad (3.04)$$

But

$$Y = 2 SD_1 \times \tan(90^\circ - \alpha) \quad (3.05)$$

where α is 45° , because in this case it applies to an application of the T.S.M. to a titration in which the indicator and titrant react with 1:1 stoichiometry.

Equations 3.04 and 3.05 combine to give,

$$\sigma = SD_2 + SD_1 \times \tan 45^\circ \quad (3.06)$$

The radii of several points in Figures 3.07 A to 3.07 E were measured and found to be about 0.04 cm. If an assumption is made that 0.04 cm is a reasonable value for SD_1 and SD_2 , then using Equation 3.06, an end point standard deviation of 0.08 cm is obtained from the considerations illustrated in Figure 3.09. It must be pointed out however, that this calculated value does not include all the sources of error. The precision of the corrected end point using the T.S.M. will also depend on a knowledge of the ratio of the conditional equilibrium constants, as was previously mentioned.

Figure 3.10 is a plot of the end point errors found by the two extrapolation procedures described earlier in this section and also of the errors found by the T.S.M. The errors obtained are plotted against the log of the ratio of the conditional equilibrium constants. The extrapolation procedures gave comparable results, with the curve from one group being slightly lower than the other. The figure shows that even with uncorrected results (curve C), the T.S.M. generally gives enormously

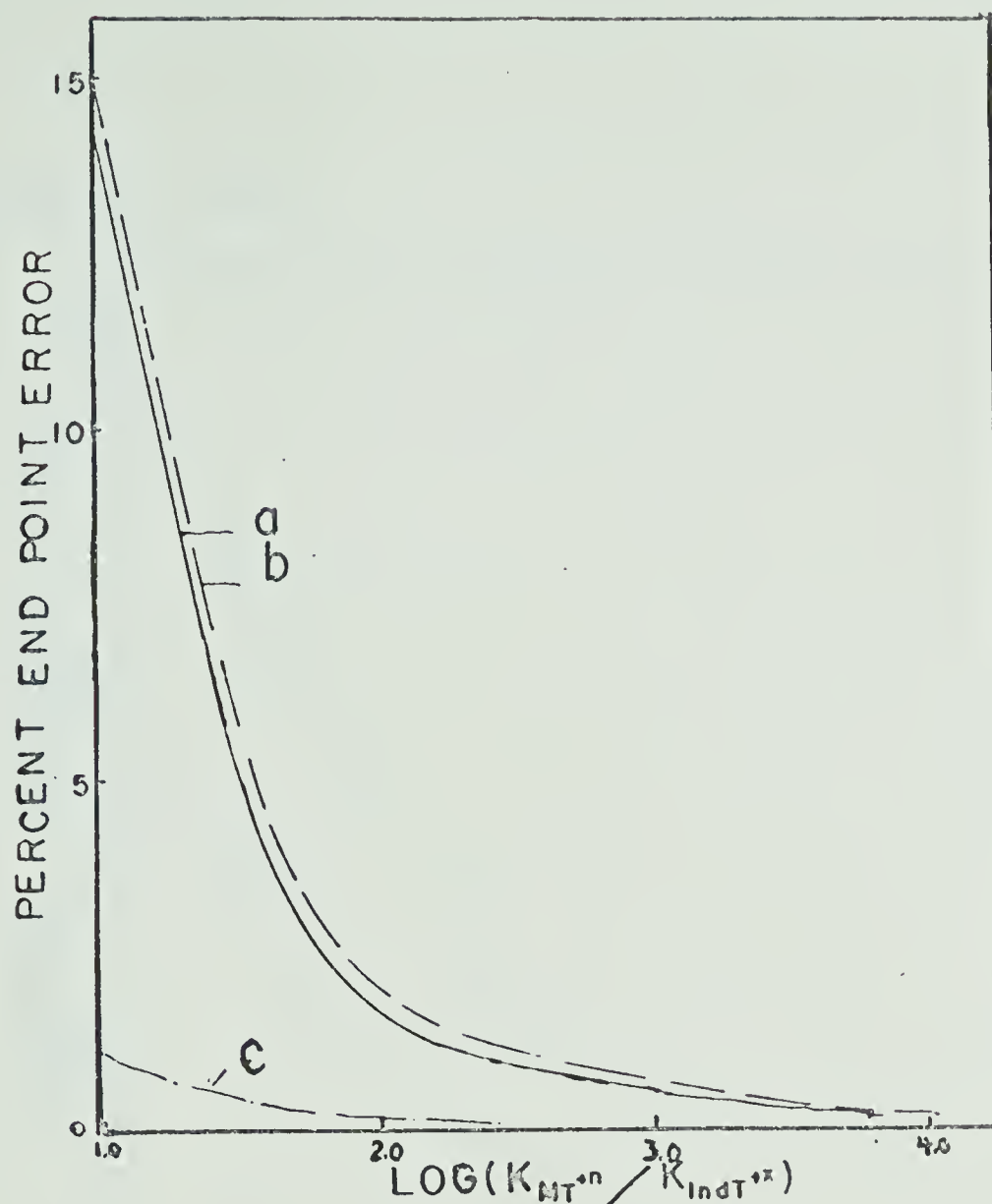


FIGURE 3.10 Comparison of the accuracy of the end points obtained by the two extrapolation techniques and the theoretical slope method. a and b, extrapolation techniques, c, T.S.M.

more accurate results than does the extrapolation method for low ratios of conditional equilibrium constants. For accurate results by the extrapolation method, the ratio of the conditional equilibrium constants should have a value greater than about 10^2 or 10^3 . For example, a ratio of $10^{1.5}$ gave an end point error of about -5 to -6 percent by the extrapolation methods, but for a ratio of 10^3 an end point error of only about -0.5 percent was obtained. For a ratio of conditional equilibrium constants of greater than about 10^3 , both the T.S.M. and the extrapolation methods gave results with

negligible error.

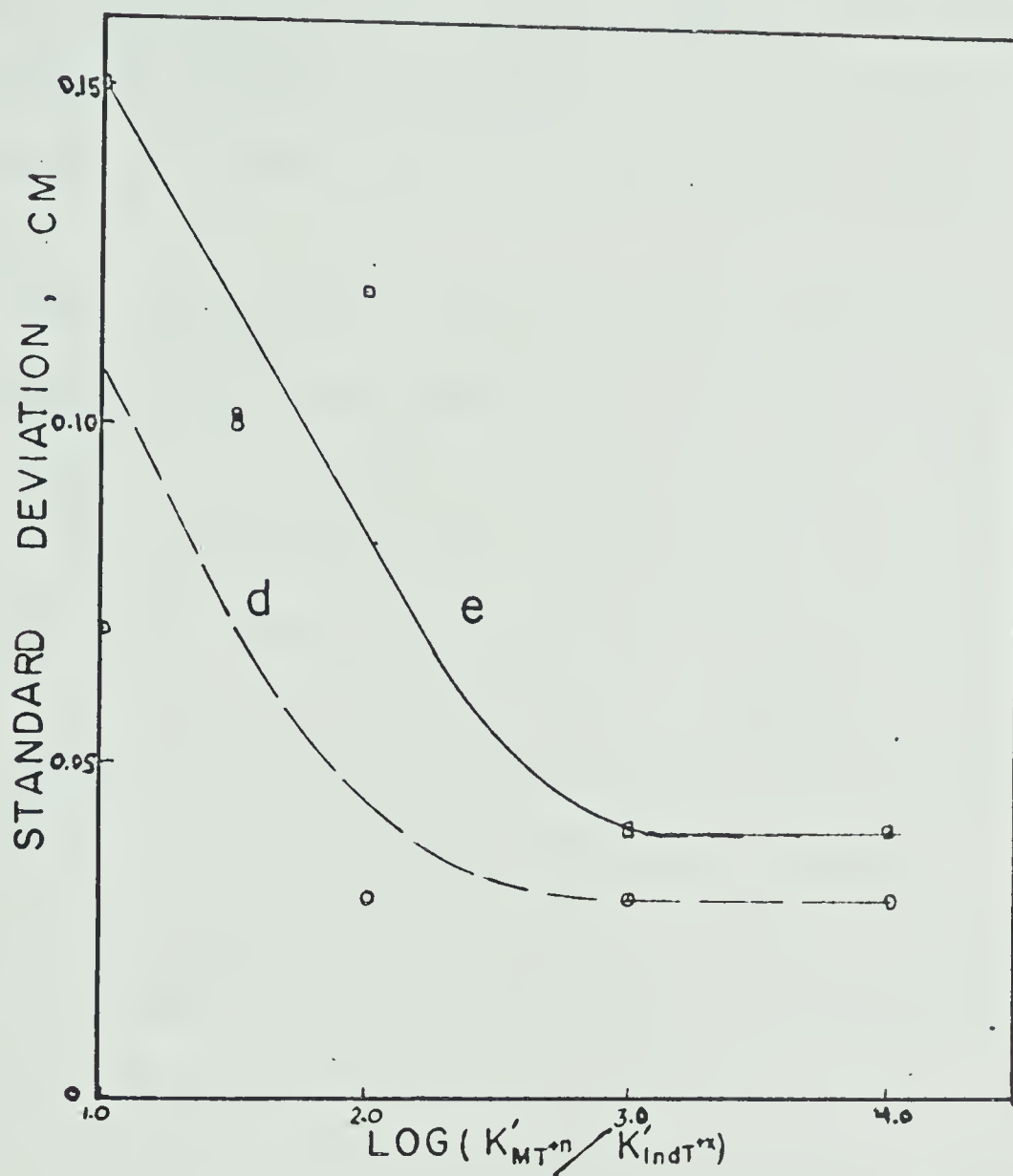


FIGURE 3.11 Comparison of the precision of the end points obtained by the two extrapolation techniques. d, first group, e, second group.

Figure 3.11 is a plot of standard deviations, instead of percent end point error, obtained by the two extrapolation methods as a function of the logarithm of the ratio of the conditional equilibrium constants. Figure 3.11 indicates that the standard deviations for the extrapolation methods decreases as the ratio of the conditional equilibrium constants becomes larger.

The figure also shows that the extrapolation procedure used by the first group gives slightly better precision than the extrapolation procedure used by the second group. This may be because the instructions in the one case appeared to be more clear cut and definite than in the other.

The trend toward lower standard deviation at large ratios of conditional equilibrium constants illustrated in Figure 3.11 would be expected because of the dependence of the end point precision on the angle, α , and the possible dependence on the length of the extrapolated line in region 2. As previously mentioned, as the ratio of the conditional equilibrium decreases, the amount of curvature in the end point region will increase. The greater the curvature, the shorter will be the straight line portion in region 2 available for extrapolation purposes and hence the lower will be the value of ϕ given by Equation 3.03. It is to be expected that the lower the value of ϕ , the greater will be the band of uncertainty, ΔL . An additional factor that is expected to influence the end point precision is the size of the points drawn in region 2. The larger the points used for extrapolation purposes, the larger should the value of the standard deviation be.

As Figure 3.10 indicates, the T.S.M. of end point detection gives more accurate results than does the extrapolation method at ratios of conditional equilibrium

constants of less than about 10^3 . It is expected, however, that the extrapolation method will give more precise results than does the T.S.M. at large ratios of conditional constants (say 10^3 or greater) but the T.S.M. will give more precise end points when the ratio is low (say $10^{1.5}$ or less). For the intermediate ratios both methods should be about as precise but as was shown, the T.S.M. results will be more accurate.

The results obtained in this section apply specifically to titration curves of the shapes and sizes investigated. Other factors such as providing more points in region 2 and increasing or decreasing the size of the points might be expected to affect the statistical evaluations. However, the trends observed would in any case be expected to be the same and hence enable the optimum conditions to be obtained. The optimum conditions for application of the extrapolation method are to have a value of α as close as possible to 90° and to have a value of ϕ as close as possible to 100 percent. A large value for ϕ suggests that experimentally, the larger the ratio of the conditional equilibrium constants, the better will be the precision.

In conclusion it may be stated that in all titration systems the T.S.M. should be considered as a means of end point detection because of its speed of application. The T.S.M. generally gives more accurate results and in the titration systems where the extrapolation method fails, the T.S.M. gives precise results as well.

3.03 SUMMARY OF STATISTICAL INVESTIGATION

In the preceding Sections 3.01 and 3.02, statistical data have been presented which indicate factors that must be considered when the extrapolation method is proposed as a precise means for end point detection. If the most precise results are to be obtained, as little extrapolation and as much interpolation as possible is desirable. It is also important that the angle between the extrapolated lines be as close to 90° as possible. These optimum conditions can, in some cases, be approached by proper choice of scale. In addition, proper choice of metal ion and/or titrant concentrations can help toward achievement of these optimum conditions.

Additional data has been presented, showing the accuracy and precision limitations of the extrapolation method of detecting end points in titration curves employing metal indicator ions. The precision and accuracy in such cases is shown to be dependent on the ratio of conditional equilibrium constants. The best precision and accuracy is obtained when the ratio of $K'_{MT} + n / K'_{IndT} + x$ is at least 10^3 . For smaller ratios the theoretical slope method is proposed as a means of detecting the end point and data has been presented comparing its accuracy to that of the extrapolation method. For larger ratios of conditional equilibrium constants the theoretical slope method is suggested as an alternative to the extrapolation method when speed is desired at the expense of precision.

4. EXPERIMENTAL RESULTS

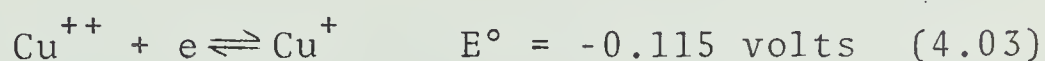
In this chapter experimental illustrations of the application of the extrapolation and theoretical slope methods of end point detection have been presented. The titrations have been carried out amperometrically and photometrically using metal indicator ions and represent systems having conditional equilibrium constant ratios ranging from 10^4 to $10^{0.1}$. Specific procedures have been presented for all titrations.

The amperometric titration of thorium using copper (II) as the amperometric indicator has been discussed first. Background chemistry of thorium, copper and EDTA has been included. Next, the results of the amperometric titrations of gadolinium, samarium, neodymium and zinc using cadmium as the amperometric indicator have been presented. The end points in these titrations have been found by the theoretical slope method. Included in this discussion is the procedure for the determination of ratios of conditional equilibrium constants. Finally results of the photometric titration of calcium using a copper ammonia complex as the photometric indicator have been shown. Included are theoretical and experimental data on the effect of ammonia concentration on the shape of the photometric titration curves.

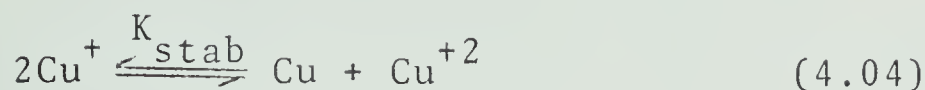
4.01 - COPPER(II) AS AN AMPEROMETRIC INDICATOR ION FOR THE DETERMINATION OF THORIUM.

General Polarography and Chemistry of Copper.

Copper (II), because it is easily reduced and forms stable complexes, is an attractive amperometric indicator. Cupric ions, in the absence of complexing agents, are reduced directly to the metallic state at a D.M.E. and only a single current voltage curve is observed. The reason for this can be seen by considering the possible electrochemical reactions of copper ions



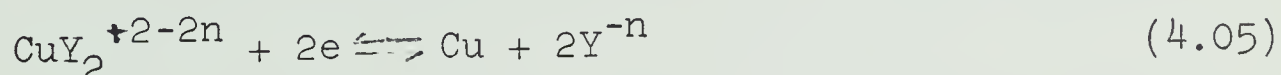
where E° is the standard potential of the reaction versus a normal calomel electrode (N.C.E.). Since the potential of the $\text{Cu}^+ \rightarrow \text{Cu(Hg)}$ reaction is more positive than that of the $\text{Cu}^{++} \rightarrow \text{Cu(Hg)}$ reaction, cuprous ions are incapable of stable existence (33, 34) at the potential at which cupric ions are reduced and disproportionate into cupric ions and metallic copper as,



The stability constant, K_{stab} , for this reaction is 10^6 (35).

In the presence of a material that forms a stable complex with cuprous ion, the standard potential of the $\text{Cu}^+ \rightarrow \text{Cu}(\text{Hg})$ reaction will be shifted in the negative direction to a greater extent than the $\text{Cu}^{++} \rightarrow \text{Cu}^+$ system. In such cases stepwise reduction occurs and a current voltage curve consisting of a double wave is observed.

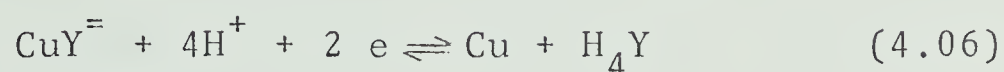
The reduction of the complexes of copper, CuY_2^{+2-2n} , with ethylenediamine, propylenediamine, diethylenetriamine or glycine produces a single wave corresponding to direct reduction to the metal, as,



From data presented by Laitinen (36) the reduction appears to proceed reversibly in all cases. He concluded that two molecules of the amine or glycine are coordinated to the cupric ion when a large excess of the complexing agent is present.

Pecsok (37) from his work on copper ethylenediamine-tetraacetate polarography, reported that the current voltage curves of the complex were well defined and nearly reversible. He found that the diffusion current, i_d , was proportional to the concentration of Cu^{+2} from

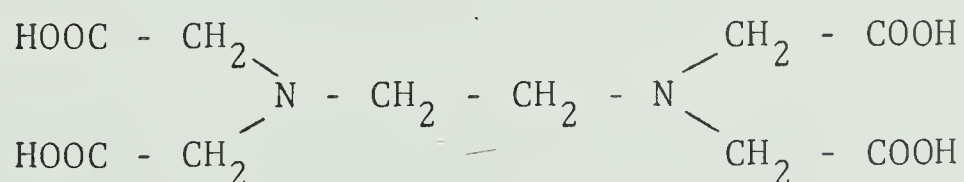
10^{-5}M to 10^{-2}M . In the region of 15°C to 35°C the temperature dependence of both diffusion current and half wave potential were linear. He reported a single wave for the reduction,



with a half wave potential, measured against a saturated calomel electrode, (S.C.E.) of -0.44 volts at pH of 6.5 to 7.0 . He found no evidence of stepwise reduction through the $+1$ state, which indicates that the $+1$ complex, CuY^{\equiv} , is unstable with respect to disproportionation of the $+2$ complex, CuY^{\equiv} , and metal, Cu .

Titration of thorium by use of copper(II) as an amperometric indicator and EDTA as the titrant.

Ethylenediaminetetraacetic acid, EDTA, because of



its multidentate character forms extraordinarily stable complexes. The ionization constants, (38), expressed as $\text{pK}'\text{s}$, for EDTA are 2.0 , 2.67 , 6.16 and 10.26 . The anion of EDTA has six sites, two basic nitrogens and four carboxylate groups, available for coordination to a metal cation in such a way that five five-membered chelate rings can be produced. Aceto complexes, themselves, are not

very stable, but the $-\text{CH}_2\text{COOH}$ grouping in molecules such as EDTA form stable complexes with all the polyvalent cations. The general tendency toward complex formation is reinforced by the chelate effect, resulting in a powerful complexing agent. EDTA forms complexes even with the lanthanide and the alkaline earth metals.

EDTA forms complexes of 1:1 stoichiometry and the formation of relatively weak 1:2 complexes is only observed with tetravalent ions. It has been studied quantitatively in the case of thorium. The tendency for thorium to take up a second EDTA molecule as measured (39) by the stability constant,

$$[\text{ThY}_2^{-4}]/[\text{ThY}][\text{Y}^{-4}] = 10^{12} \quad (4.07)$$

is small compared with the tendency (40) to form the normal complex, ThY , where

$$[\text{ThY}]/[\text{Th}^{+4}][\text{Y}^{-4}] = 10^{23.2} \quad (4.08)$$

The stability constant of the copper(II) - EDTA complex is given (40) as $10^{18.8}$

$$[\text{CuY}^-]/[\text{Cu}^{+2}][\text{Y}^{-4}] = 10^{18.8} \quad (4.09)$$

Several methods have been proposed for the determination of thorium. Blaedel and Malmstadt (41) described an accurate, indirect volumetric method using high frequency titrimetry. Fritz and Ford (42) accurately titrated small amounts of thorium (11 to 150 mg)

with EDTA using a visual indicator. Malmstadt and Gohrbant (43), using a spectrophotometric method with copper(II) as the indicator ion and EDTA as the titrant, were able to determine 20 to 70 mg of thorium. Goldstein, Manning and Zittel (44), using platinum foil as the indicator electrode and iron(II) as the indicator ion determined as little as 6.5 mg with a relative standard deviation of 2%. Gordon and Stine (45) determined as little as 10 mg of thorium in monazite sand by amperometric titration with ammonium molybdate using a dropping mercury electrode.

Amperometry, using a rotating platinum electrode (R.P.E.) with its enhanced sensitivity, has proven ideally suited for the determination of minor constituents in the presence of less easily reduced major constituents. In this study it is proposed as a simple and rapid analytical method for determination of microgram amounts of thorium using copper(II) as the amperometric indicator ion and EDTA as the titrant. Copper(II) is an attractive possibility for an amperometric indicator because it is easily reduced and forms a stable complex with EDTA.

When the tetravalent anion of EDTA (Y^{-4}) is added to a solution of thorium and copper(II) in a monochloroacetic acid-monochloroacetate buffer of pH 3.1, the reactions are as shown in Figure 4.01. Prior to the equivalence point the important reactions are those shown in the upper part of Figure 4.01. At or near

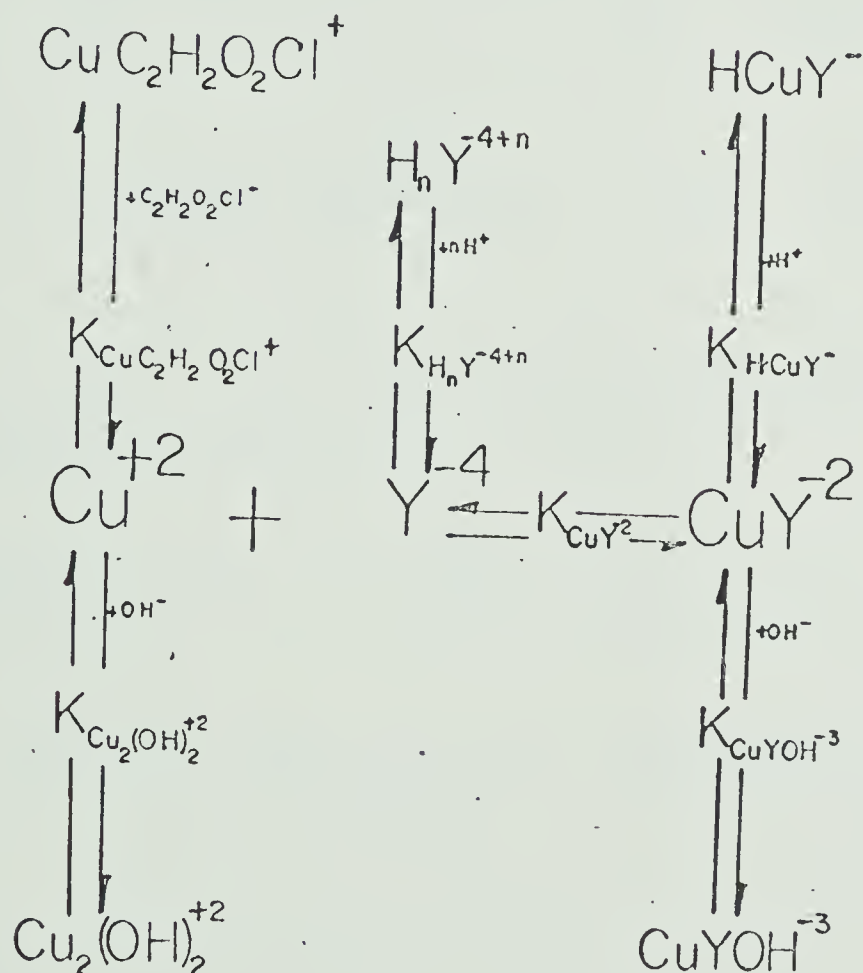
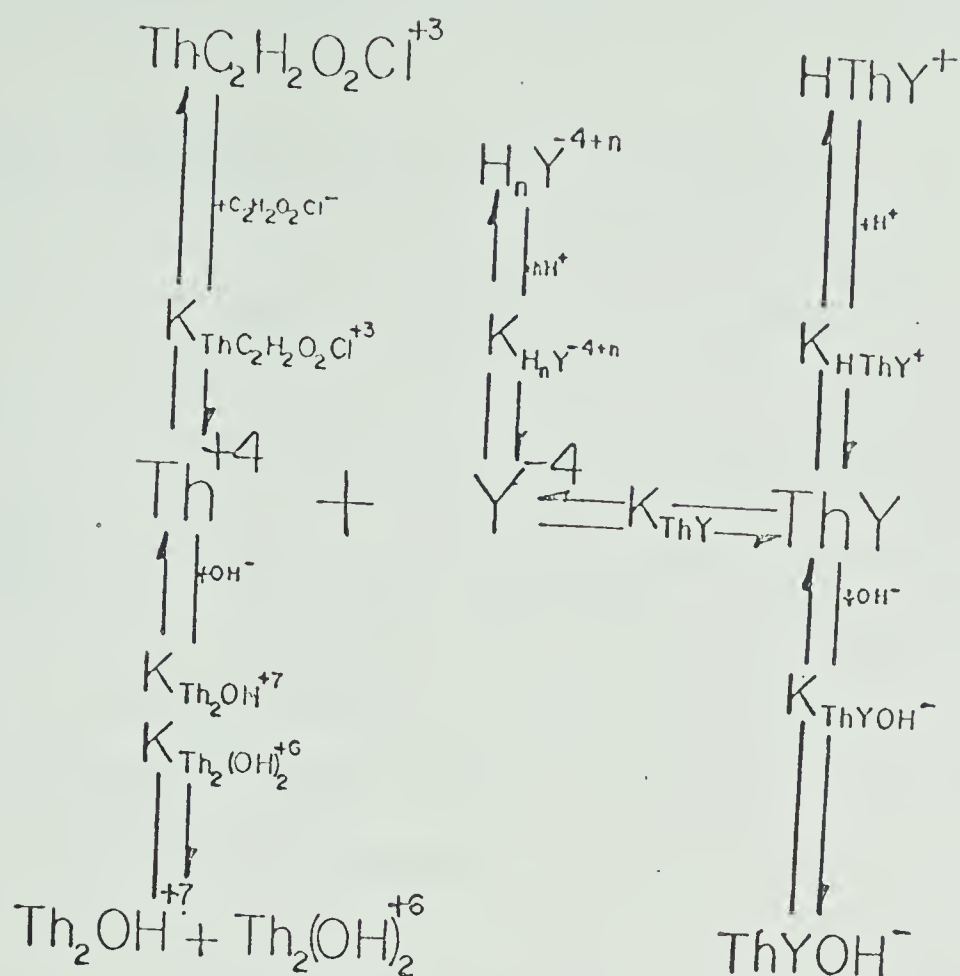
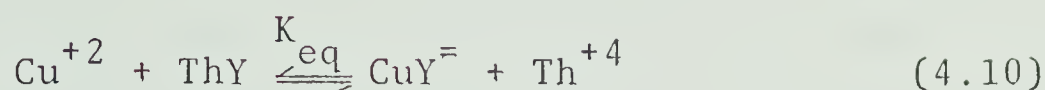


Figure 4.01 Upper, equilibria involving thorium, EDTA, hydrogen ion, hydroxyl ion and chloroacetate ion; lower, equilibria involving copper(II), EDTA, hydrogen ion, hydroxyl ion and chloroacetate ion.

the equivalence point the equilibrium



must be considered. In this reaction K_{eq} is equal to $\frac{K'_{\text{CuY}^-}}{K'_{\text{ThY}}}$, where K'_{ThY} and K'_{CuY^-} are the conditional equilibrium constants. They are functions of pH and the concentrations of the auxiliary complexing agents. The conditional constants are calculated, according to Laitinen (14), in the following manner.

$$K_{\text{ThY}} = \frac{[\text{ThY}]}{[\text{Th}^{+4}][\text{Y}^{-4}]} = 10^{23.2}; \quad K_{\text{CuY}^-} = \frac{[\text{CuY}^-]}{[\text{Cu}^{+2}][\text{Y}^{-4}]} = 10^{18.8} \quad (4.11)$$

$$K'_{\text{ThY}} = \frac{C_{\text{ThY}}}{C_{\text{Th}^{+4}} \cdot C_{\text{Y}^{-4}}}; \quad K'_{\text{CuY}^-} = \frac{C_{\text{CuY}^-}}{C_{\text{Cu}^{+2}} \cdot C_{\text{Y}^{-4}}} \quad (4.12)$$

where $C_{\text{Th}^{+4}}$ is the total concentration of thorium not complexed with EDTA and is equal to

$$\begin{aligned} & [\text{Th}^{+4}] + [\text{ThC}_2\text{H}_2\text{O}_2\text{Cl}^{+3}] + [\text{Th}_2\text{OH}^{+7}] + [\text{Th}_2(\text{OH})_2^{+6}] \\ &= [\text{Th}^{+4}] [1 + [\text{C}_2\text{H}_2\text{O}_2\text{Cl}^-] K_{\text{ThC}_2\text{O}_2\text{H}_2\text{Cl}^{+3}} + [\text{Th}][\text{OH}] K_{\text{Th}_2\text{OH}^{+7}} + [\text{Th}][\text{OH}]^2 \cdot K_{\text{Th}_2\text{OH}_2^{+6}}] \\ &= [\text{Th}^{+4}] / \beta_{\text{Th}} \end{aligned}$$

where β_{Th} is the fraction of thorium ion not complexed with EDTA and is present as the aquated ion. Similarly, C_{Cu}^{+2} is the total concentration of copper not complexed with EDTA and is equal to $[Cu^{+2}]/\beta_{Cu}^{+2}$ where

$$\frac{1}{\beta_{Cu}^{+2}} = 1 + [C_2H_2O_2Cl^-]K_{CuC_2H_2O_2Cl^+} + [Cu^{+2}][OH^-]^2 \cdot K_{Cu_2(OH)_2}$$

In this expression β_{Cu}^{+2} is the fraction of copper ion not complexed with EDTA and is present as the aquated ion. C_Y^{-4} is the total concentration of EDTA not complexed with metal ions and is equal to $[Y^{-4}]/\alpha_4$, where α_4 is the fraction of free EDTA present as the tetravalent anion. C_{ThY} is the total concentration of thorium complexed with EDTA and is equal to

$$[ThY] + [HThY^+] + [ThYOH^-] = [ThY]/\beta_{ThY}$$

where β_{ThY} is the fraction of ThY that is present as the aquated species. $C_{CuY}^=$ is the total concentration of copper complexed with EDTA in the mole ratio of 1:1. It is equal to

$$[CuY^=] + [HCuY^-] + [CuYOH^=] = [CuY^=] \{ 1 + [H^+]K_{HCuY^-} + [OH^-] \cdot K_{CuYOH^=} \} = [CuY^=]/\beta_{CuY}^=;$$

where $\beta_{CuY}^=$ is the fraction of $CuY^=$ that is present as the aquated species.

Equation 4.12 may be changed into the form

$$K'_{ThY} = K_{ThY} \cdot \frac{\alpha_4 \cdot \beta_{Th}^{+4}}{\beta_{ThY}} \quad \text{and} \quad K'_{CuY} = K_{CuY} \cdot \frac{\alpha_4 \beta_{Cu}^{+2}}{\beta_{CuY}^=} \quad (4.13)$$

or

$$\log K'_{ThY} = \log K_{ThY} + \log \alpha_4 + \log \beta_{Th}^{+4} - \log \beta_{ThY} \\ \text{and} \quad (4.14)$$

$$\log K'_{CuY} = \log K_{CuY} + \log \alpha_4 + \log \beta_{Cu}^{+2} - \log \beta_{CuY}^= \quad (4.15)$$

Calculations of β and α values at pH 3.0 using a chloroacetate ion concentration of $6 \times 10^{-3} M$ give:

$$\log \alpha_4 = -10.60$$

$$\log \beta_{Cu}^{+2} = -0.08$$

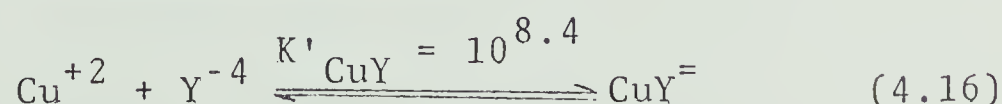
$$\log \beta_{CuY}^= = -0.30$$

$$\log \beta_{Th}^{+4} = -0.82$$

$$\log \beta_{ThY} = 0$$

K'_{ThY} and K'_{CuY} are calculated to be $10^{11.78}$ and $10^{8.42}$ respectively. Therefore $K_{eq} = 10^{-3.4}$. The value of K_{eq} indicates that reaction (4.10) does not proceed appreciably to the right.

Following the equivalence point, the principal equilibrium to be considered is



As indicated by the large value of the equilibrium constant, copper(II) concentration should decrease linearly with the amount of excess EDTA added.

Experimental

Titration were carried out in a 90 ml beaker (see Figure 4.02). This was covered with a rubber stopper carrying a nitrogen bubbler and a sintered glass junction to a saturated calomel electrode (S.C.E.). Holes were also provided for the rotating platinum electrode and the tip of a 5 ml microburet. A Metrohm Polarecord Model E261 polarograph was used primarily as a recording galvanometer. This instrument has a high sensitivity (10^{-4} μ a/mm) which made it possible to detect small changes in the concentration of copper.

In all solutions deionized water was used to eliminate reducible interferences.

A 10^{-2} M stock solution of thorium nitrate was prepared from Fisher Certified Reagent thorium nitrate. It was standardized by precipitating as thorium oxalate, igniting and weighing as thorium oxide. EDTA solutions were prepared from Fisher Certified disodium ethylenediaminetetraacetate and standardized against magnesium iodate (46). A 10^{-3} M copper solution was prepared by dissolving a weighed amount of copper wire in a small

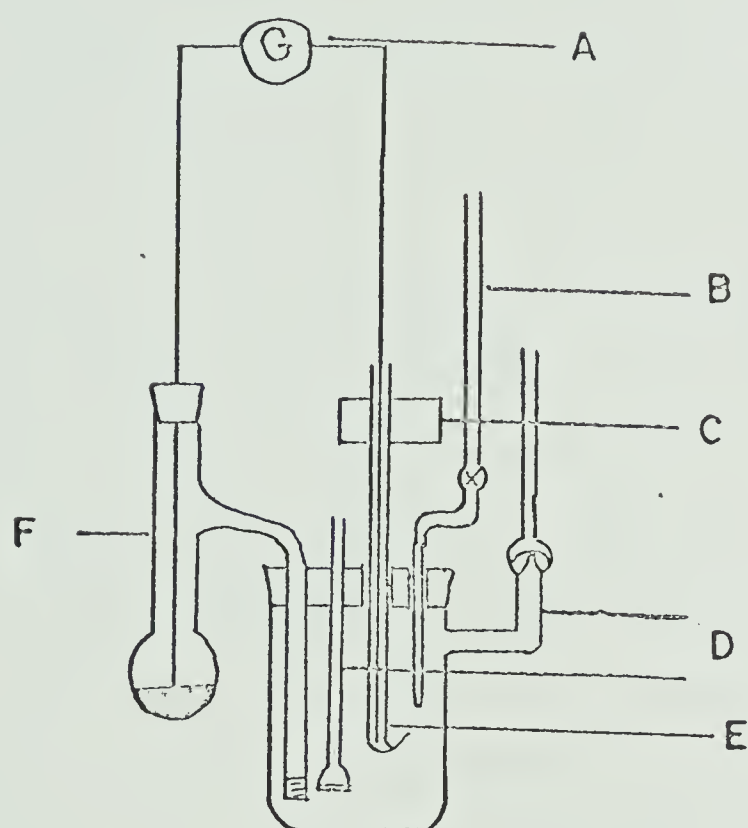


FIGURE 4.02 Amperometric titration apparatus for the determination of thorium using copper(II) as the amperometric indicator. A, scale and lamp galvanometer; B, buret; C, synchronous rotator; D, nitrogen inlets; E, platinum indicator electrode; F, saturated calomel reference electrode.

amount of concentrated nitric acid and diluting to volume. Solutions were buffered by mixing appropriate amounts of 0.15M monochloroacetic acid and 0.2M sodium hydroxide.

Prior to each titration the electrode was cleaned with warm aqua regia. It was then rinsed several times with water and polarized at 0.0V vs. S.C.E. for approximately ten minutes in the solution to be titrated.

Aliquots of thorium and copper II solutions were introduced into the reaction cell along with 5 ml of 0.15M chloroacetic acid. The pH of the system was adjusted with the aid of a pH meter to the desired value (3.1 ± 0.1) by the addition of 0.2M NaOH. The solution was diluted to approximately 70 mls and then deaerated with nitrogen for approximately five minutes. Following this, by means of a two way stopcock, nitrogen was passed over the surface. EDTA was then added in suitable increments and the current recorded at a potential of 0.0 volts vs. S.C.E. The sensitivity, from one experiment to another, was poorly reproducible ($\pm 30\%$) and dependent on electrode pretreatment. However, changes in sensitivity for a given run did not affect the linearity between current and copper concentration nor appreciably affect the precision of the end points obtained.

Results Obtained and Problems Encountered

The initial approach to this problem of titrating

thorium amperometrically using copper(II) as the amperometric indicator and EDTA as the titrant was to use a constant flow buret and record the titration curve automatically with the Polarocord. However, this approach was unsuccessful. Positive errors were consistently obtained and were attributed to the kinetics of the reactions. This was overcome by performing the titrations manually, using the PolarEcord as a recording galvanometer. In some cases it was found that the best results were obtained when the electrode was cleaned with warm aqua regia prior to each titration.

A typical current voltage curve obtained for copper(II)-reduction in the solution to be titrated is given in Figure 4.03. The optimum voltage for the amperometric

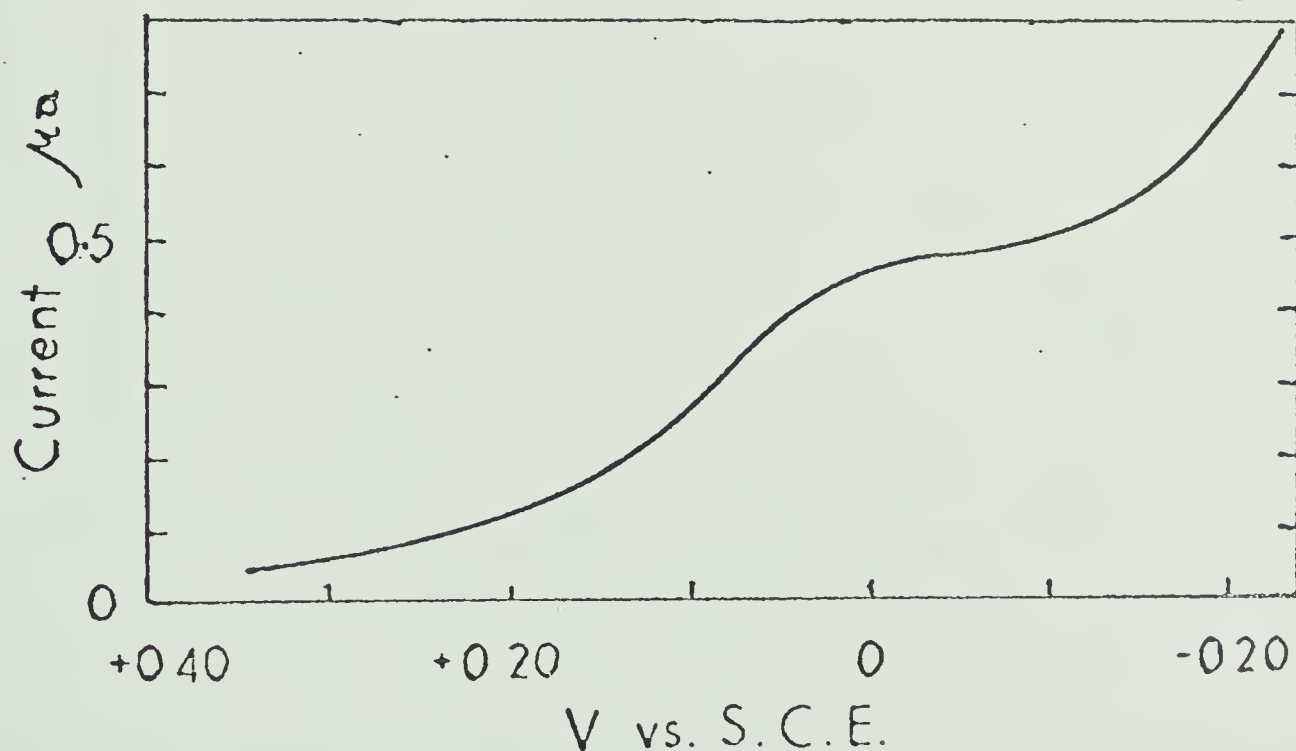


Figure 4.03 Current voltage curve of 7.8×10^{-5} M copper(II) and 7.1×10^{-4} M thorium solution. $pH = 3.1 \pm 0.1$.

titration was chosen to be 0 volts vs. S.C.E. The magnitude of the diffusion current was not found to be reproducible to any better than approximately ± 5 percent. Investigation of the relationship between diffusion current and mole ratio of EDTA to copper(II) indicated a stoichiometric relationship of 1:1 under the experimental conditions, (Figure 4.04). The current voltage curves were

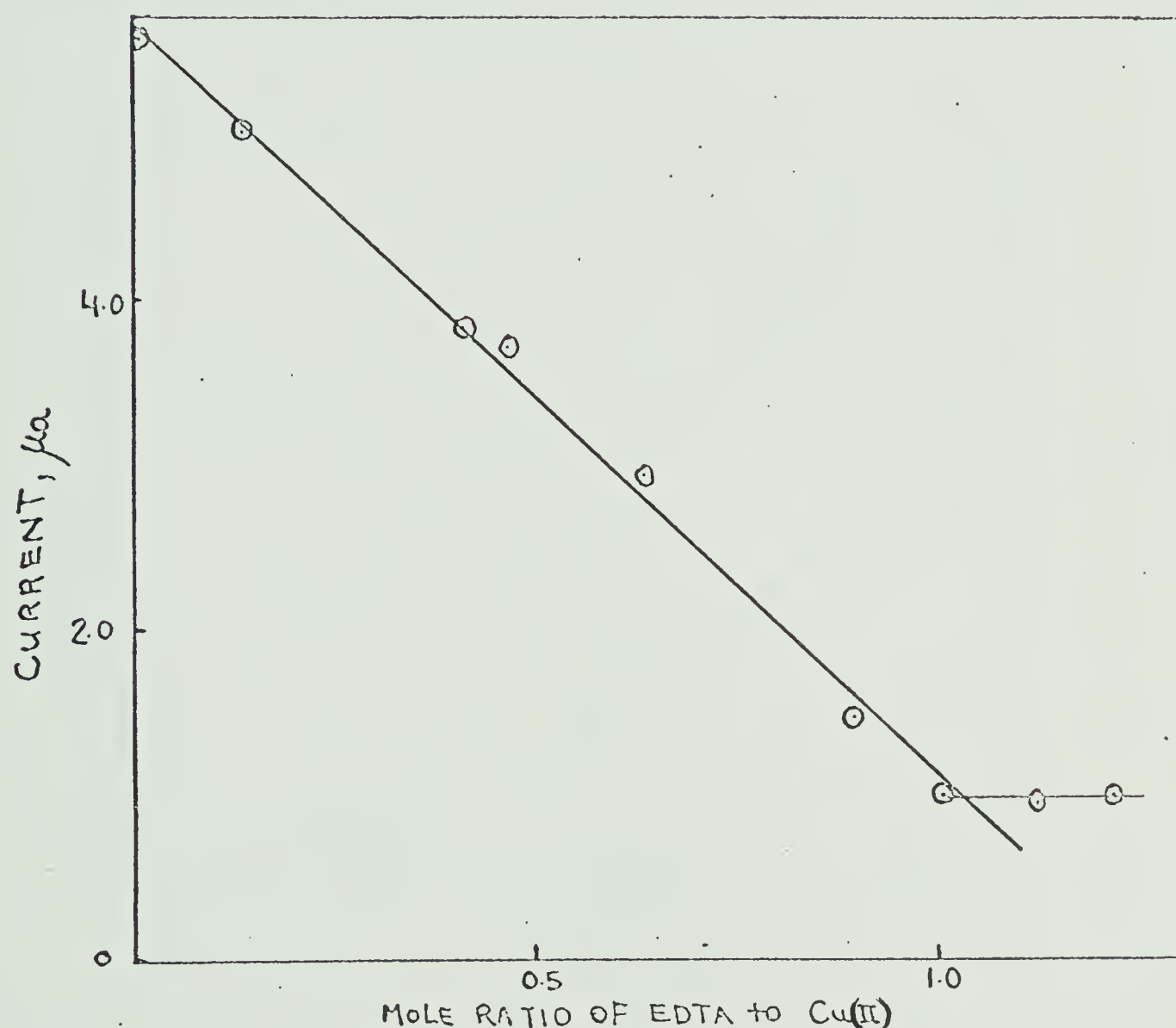


Figure 4.04 Plot of Cu(II) diffusion current versus mole ratio of EDTA to Cu(II). 6.43×10^{-3} M Cu(II) titrated with 1.024×10^{-2} M EDTA at pH 3.1. Potential of 0.0 volts vs. S.C.E. R.P.E. used.

found to be irreversible and the current measurements were made at 0.0 volts vs. S.C.E. using a rotating platinum electrode, (R.P.E.). It was found that the diffusion current decreased considerably (~30%) upon addition of thorium to a solution of copper(II) in an amount to give a $C_{Th}^{+4}:C_{Cu}^{+2}$ ratio of less than 8 as can be seen in Figure 4.05. Breckenridge (47) in his work

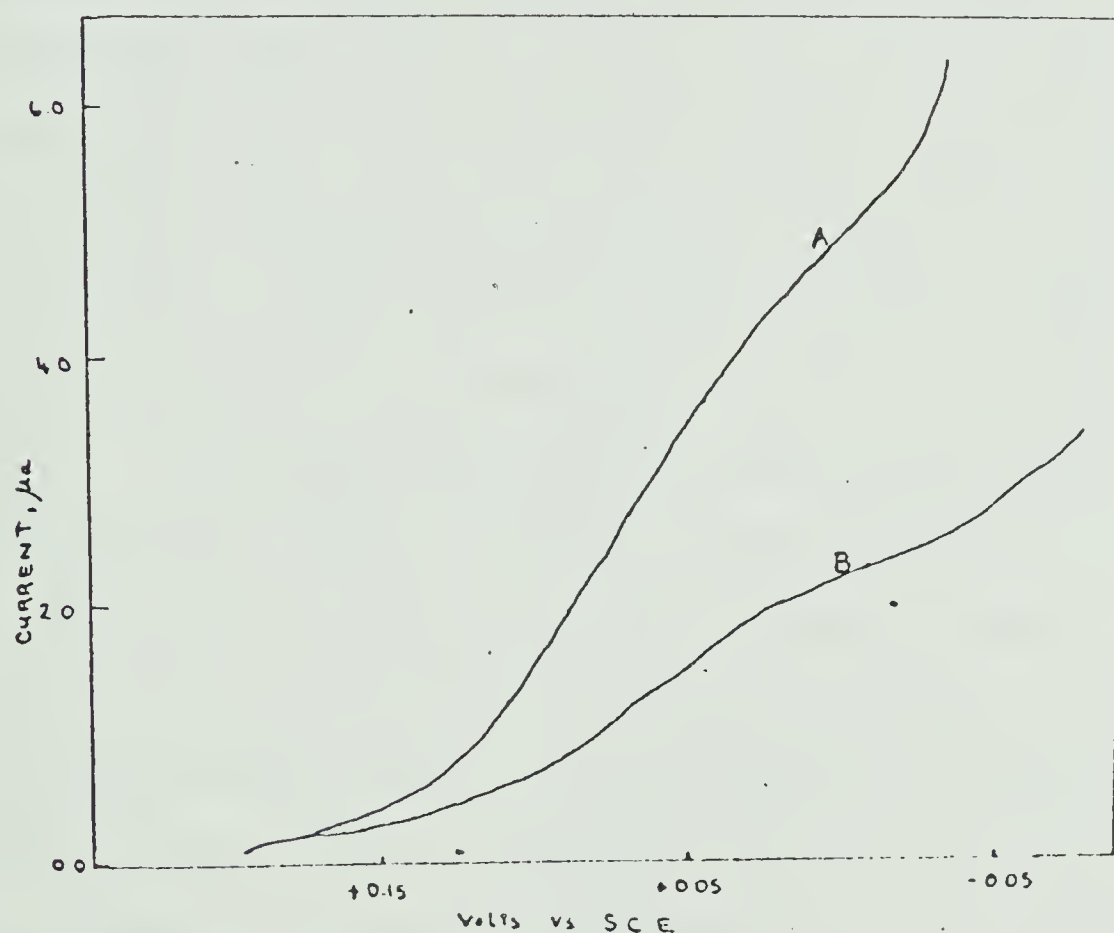


Figure 4.05 Current voltage curves of, A, 7.54×10^{-3} M copper(II) at pH of 3.1; B, 7.54×10^{-3} M copper(II) and 9.82×10^{-3} M thorium at pH of 3.1.

on the effect of thorium on the ferric-ferrous couple observed the same depression effect. He speculated that it was due to the formation of an iron-thorium complex which decreased the amount of Fe^{+3} available for reduction. However, he observed no significant trend to substantiate this. He concluded that the primary effect of thorium is the reduction of the exchange current for the ferric-ferrous couple. He postulated that the principal cause of this effect is the high charge carried by the thorium cation. When a solution containing thorium and copper, in a ratio of less than 8, was titrated a small maximum occurred in the titration curve immediately prior to the equivalence point. (See experimental point immediately prior to end point in Figure 4.06, A). This maximum was observed to vary with the mole ratio of thorium to copper and with the extent of electrode cleaning prior to each titration. Maintenance of the ratio of thorium to copper at a value greater than 8 ensured a sharp break in the curve.

Figure 4.06 shows experimental and calculated titration curves for several titrations of 1.660 milligrams of thorium. The ordinate is the diffusion current expressed in microamps and is proportional to the copper concentration. When the $\text{C}_{\text{Th}}^{+4}:\text{C}_{\text{Cu}}^{+2}$ ratio is high

LE 4.01 RESULTS OF TITRATING VARIOUS AMOUNTS OF THORIUM WITH
 $2 \times 10^{-2}M$ TO $0.04 \times 10^{-2}M$ EDTA SOLUTIONS

Thorium Present mg	[Th]/[Cu]	Thorium Found mg ^x	Relative Standard Deviation, percent
11.11	6.8	11.15 (4)	0.4
11.11	13.6	11.10(10)	0.4
11.12	26.0	11.23 11.25 10.93 11.16	
11.12	106.0	11.10 11.01 11.09	
6.63	4.1	6.88 (2)	
	5.4	6.86 (3)	3.1
	8.2	6.67 (9)	0.6
	16.3	6.63(10)	0.2
6.68	16.0	6.70 6.70 6.74	
6.68	64.0	6.70 6.68	
1.67	4.0	1.70 1.70 1.78	
1.66	8.1	1.66 (8)	1.0
1.67	16.0	1.67 1.66 1.61	
0.664	6.47	0.671(8)	1.5
	12.47	0.663(7)	1.5
0.134	0.32	0.142 0.156 0.148	
0.134	1.3	0.139 0.145 0.142	
0.133	11.5	0.130(8)	0.8

* Some results are averages of several titrations - equal to the number in brackets.

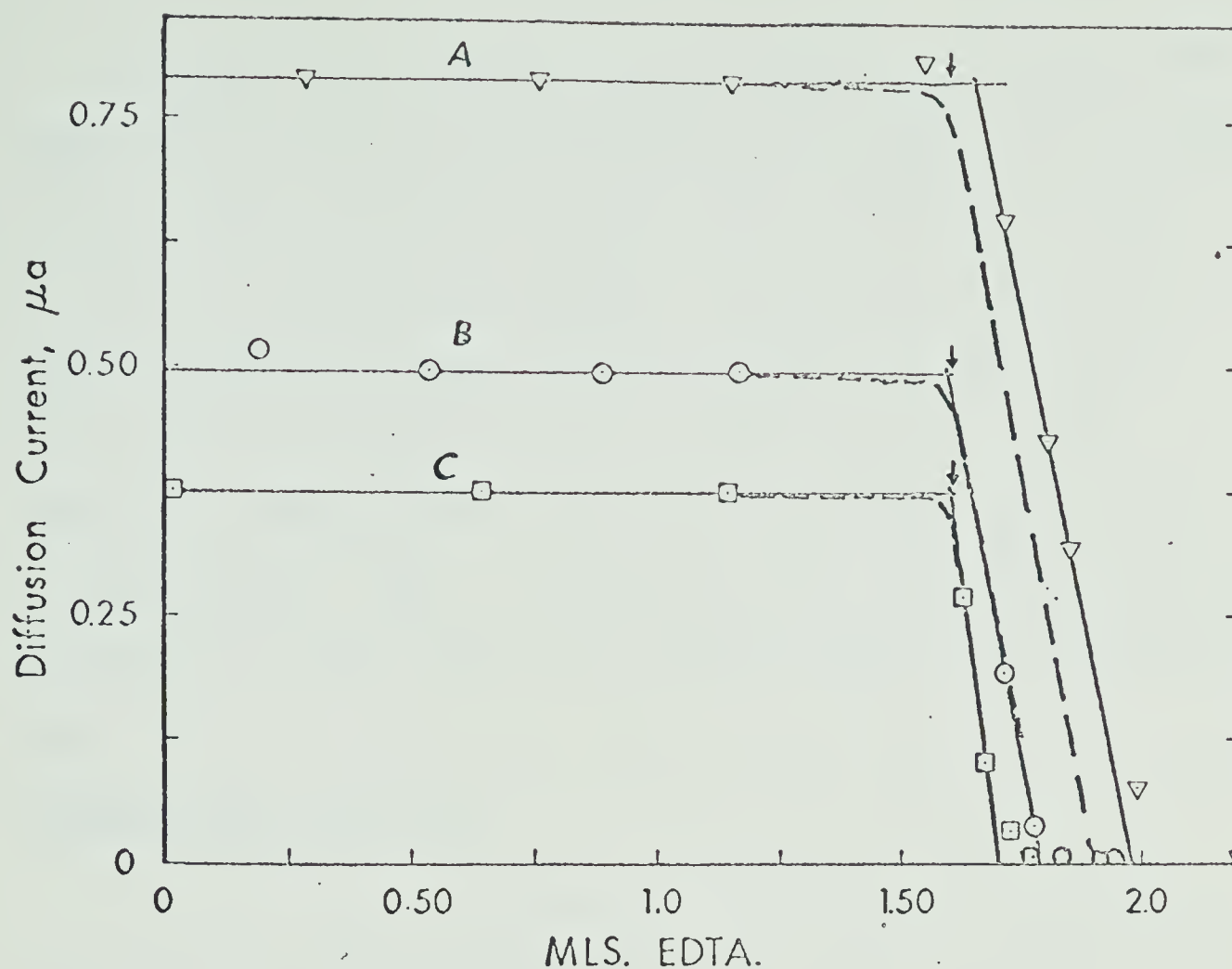


Figure 4.06 Titration curves of 1.66 milligrams of thorium with 4.461×10^{-3} M EDTA. The arrows indicate the theoretical end points at 1.602 mls. Curves A, B and C refer to thorium to copper ratios of 5.4, 8.2 and 16.3. Dotted lines are the calculated theoretical curves.

the experimental end point agrees with the theoretical end point (Figure 4.06 B, 4.06 C) but deviates when the ratio is low (Figure 4.06 A). Confirmation of the importance of $C_{Th}^{+4}:C_{Cu}^{+2}$ ratio is shown in Table 4.01. As the ratio is decreased, the absolute error and relative standard deviation both increase. The results for the determination of 6.63 mg of thorium illustrate this trend most clearly.

Although the reason is not clear, it was found that with larger amounts of thorium (6 to 11 mg) the electrode did not need cleaning as often (every fifth titration) to obtain reproducible results. However, at the lower thorium concentrations (1.6 to 0.13 mg) it was found that if the electrode was not cleaned prior to each titration, the absolute error increased with the number of titrations. This is possibly due to the slow adsorption of thorium on the electrode surface when the concentration is low.

Recommended Procedure

To the sample containing 5 to 10 mg of thorium add 5 mls of 0.15M monochloroacetic acid and 4 mls of 5×10^{-4} M solution of copper II. Dilute to 70 or 80 milliliters. With a pH meter, adjust the pH to 3.1 ± 0.1 by the addition of 0.2M NaOH. Apply a potential of 0 volts vs. S.C.E. to a clean R.P.E. Titrate with standard 2×10^{-2} M EDTA using a 5 ml microburet. Read the current with an instrument having a sensitivity of about 0.1 μ a/cm. Correct for the dilution effect, if necessary, and determine end point by extrapolation of the two straight lines obtained when diffusion current is plotted against volume.

Interferences

Theoretically, interference may result from any cation which complexes or precipitates EDTA; as may any anion which reacts with thorium or copper(II). With a solid electrode, adsorption phenomena may also cause

error. The effects of several potential interferences was investigated at a wide range of concentrations with a mole ratio of thorium to copper of about 16. Na^+ , Li^+ , K^+ , Mg^{+2} do not interfere when present in amounts up to at least 100 times the weight of thorium. Cd^{+2} , Zn^{+2} , La^{+3} , Pb^{+2} , Al^{+3} interfere in amounts of 100 and 10 times the weight of thorium but cause little error at the 0.5 fold level. These cations interfere when present in large amounts because the stability of their EDTA complexes approaches that of the copper-EDTA complex. Ag^+ interferes at the 10 and 100 fold levels but not at the 0.5 fold level, mainly because it is more easily reduced than Cu(II) . This means that with Ag^+ present the diffusion current is larger throughout the entire titration and hence the end point cannot be precisely located. Ba^{+2} , Ca^{+2} , Cl^- , $\text{SO}_4^{=}$, $\text{SO}_3^{=}$ and $\text{PO}_4^{=}$ also interfere at the 10 and 100 fold levels for reasons that are not evident at present. Fe^{+3} , Cr^{+3} , Ni^{+2} , ZrO^{++} , Sn^{+2} interfere at all levels. These cations react with EDTA to form complexes with stabilities that approach that of the thorium-EDTA complex. Ce^{+3} , Mn^{+2} and Co^{+2} interfere at all levels. The interference in these cases is probably the result of adsorption on the electrode (47). Bi^{+3} is intolerable at all levels also and appears to be a combination of adsorption and EDTA stability considerations. The diffusion current in the presence of this cation is low.

4.02 CADMIUM AS AN AMPEROMETRIC INDICATOR FOR THE DETERMINATION OF GADOLINIUM, SAMARIUM, NEODYMIUM AND ZINC, USING EDTA AS THE TITRANT.

Cadmium is not suitable as an amperometric indicator with a rotating platinum electrode mainly because it is not reduced easily enough. The reaction, $\text{Cd}^{+2} + 2\text{e} \rightleftharpoons \text{Cd}$ occurs at about -0.7 volts versus S.C.E. at a pH of 4.2. Copper (II) is a more attractive indicator ion because it is reduced at a more positive potential, as has been discussed. However, for the determination of Gd^{+3} , Sm^{+3} , Nd^{+3} as Zn^{+2} with EDTA as the titrant, cadmium is a more useful indicator ion when a D.M.E. is used. According to data obtained by Schwarzenbach (31), the equilibrium constant of the EDTA complex with copper is larger than the equilibrium constants of Gd^{+3} , Sm^{+3} , Nd^{+3} and Zn^{+2} complexes with EDTA. Therefore the amperometric titration of these ions with Cu^{+2} as the amperometric indicator will not give an end point that corresponds to the amount of the metal ion present. Schwarzenbach also found that the complex of Cd^{+2} with EDTA is less stable than the complex of Sm^{+3} , Gd^{+3} , Nd^{+3} and Zn^{+2} with EDTA. As mentioned previously, this is an important feature of a satisfactory amperometric indicator.

Pribil and Matyska (48) studied the amperometric titration of cadmium with disodium ethylenediaminetetraacetate

using the D.M.E. as an indicator electrode but gave no details. Tanaka (49) also investigated the amperometric titration of cadmium with EDTA and the effect of the kinetic current on the titration curve was discussed. They found an enhanced diffusion current corresponding to free cadmium in solution when there was enough EDTA to completely react with all of the cadmium. They explained the increase in current, corresponding to the reduction of free cadmium ion, as being due to the dissociation of CdY^- on the surface of the mercury to form the free cadmium ion in the course of electrolysis. They obtained satisfactory agreement between experimental end points and equivalence points when the solution contained 0.001% gelatin. When the titrations were carried out in the absence of gelatin, the experimental end points were somewhat greater than the stoichiometrical ones because of the kinetic current due to the dissociation of the complex.

Schmid and Reilley (50) also examined the polarography of cadmium-EDTA and concluded that in the pH region of 1 to 4 a kinetic wave attributed to free cadmium ions occurs. In the pH region from 2 to 5 a second wave occurs. This second wave is due to the reduction of CdYH^- and its height is controlled by the rate of recombination of CdY^- with hydrogen ions. In the pH region above 5 the wave height of this second wave is independent of pH but is strongly dependent on

the kind, charge and concentration of the inert cations in solution. They attributed this effect to the formation of an ion pair between CdY^{\equiv} and the cation or to the formation of an activated bridge complex involving the surface of the mercury electrode, the cation, and CdY^{\equiv} . They found no spectrophotometric evidence for the formation of ion pairs in solution.

Apparatus and Procedure for Determination of Ratio of Conditional Equilibrium Constants

The experimental apparatus used is shown in Figure 4.07. The indicator electrode used was a D.M.E. Polarographic

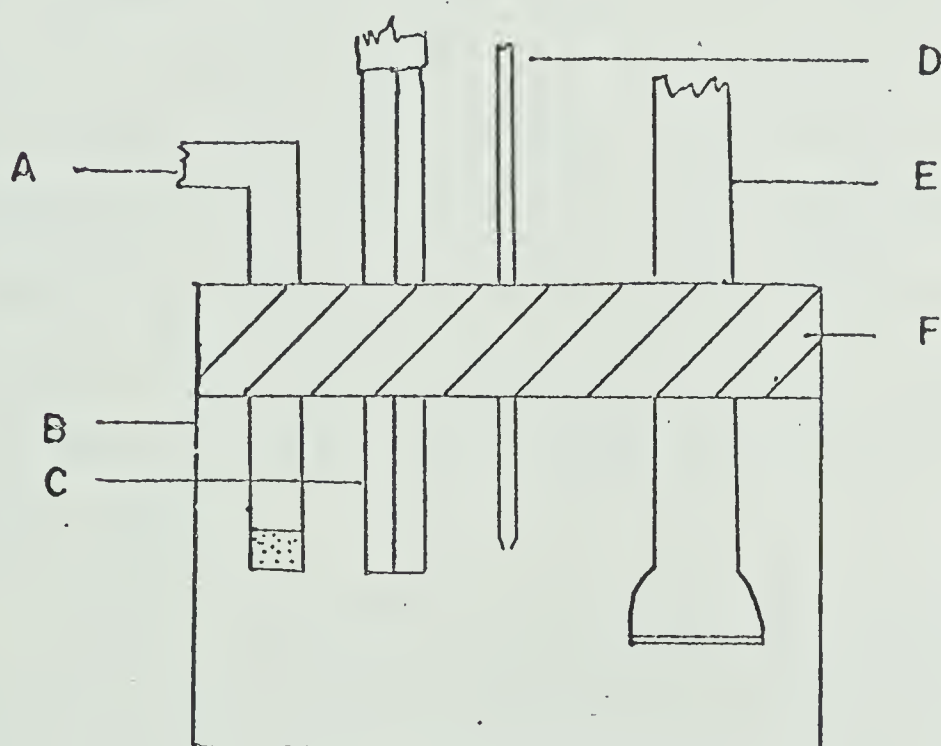


Figure 4.07 Titration cell used for amperometric titrations and equilibrium constant determinations using a dropping mercury electrode. A, S.C.E.; B, glass cell; C, D.M.E.; D, tip of microburet; E, nitrogen bubbler; F, 4 hole rubber stopper. The cell was immersed in a constant temperature bath.

graphic measurements were made with the aid of the Metrohm Polarecord E261. The polarographic cell illustrated in Figure 4.07 was maintained at a temperature of $21.0^{\circ} \pm 0.02^{\circ}\text{C}$ by a Colora Ultra thermostat circulating bath. All solutions were prepared with deionized water.

A $2 \times 10^{-2}\text{M}$ stock solution of cadmium nitrate was prepared from Fisher Certified Reagent cadmium nitrate and was standardized by precipitation and weighing (51) as cadmium ammonium phosphate. Stock solutions of samarium nitrate, gadolinium nitrate and neodymium nitrate were prepared from Alfa Inorganic reagents (99.9% pure) to concentrations of $1.7 \times 10^{-2}\text{M}$. The concentrations were checked by precipitation as hydroxides and weighing, after ignition, as the oxides. A $2 \times 10^{-2}\text{M}$ stock solution of zinc nitrate was prepared from Fisher Certified reagent zinc nitrate and was standardized by precipitation (52) and weighing as zinc ammonium phosphate. A 10^{-1}M stock solution of EDTA was prepared from Fisher certified disodium ethylenediaminetetraacetate and standardized against magnesium iodate (46).

Before a detailed experimental procedure can be specified the ratio of conditional equilibrium constants should be measured. Current voltage curves were obtained for Cd^{+2} reduction in solutions of the metal ions to be titrated at a pH of 4.2, ionic strength of 0.1, temperature of 21°C , and 0.001% gelatine. These

curves indicated that the diffusion current of Cd^{+2} can be obtained at -0.7 volts versus S.C.E. Figure 4.08 is the curve obtained for the Cd^{+2} reduction in the presence of Zn^{+2} .

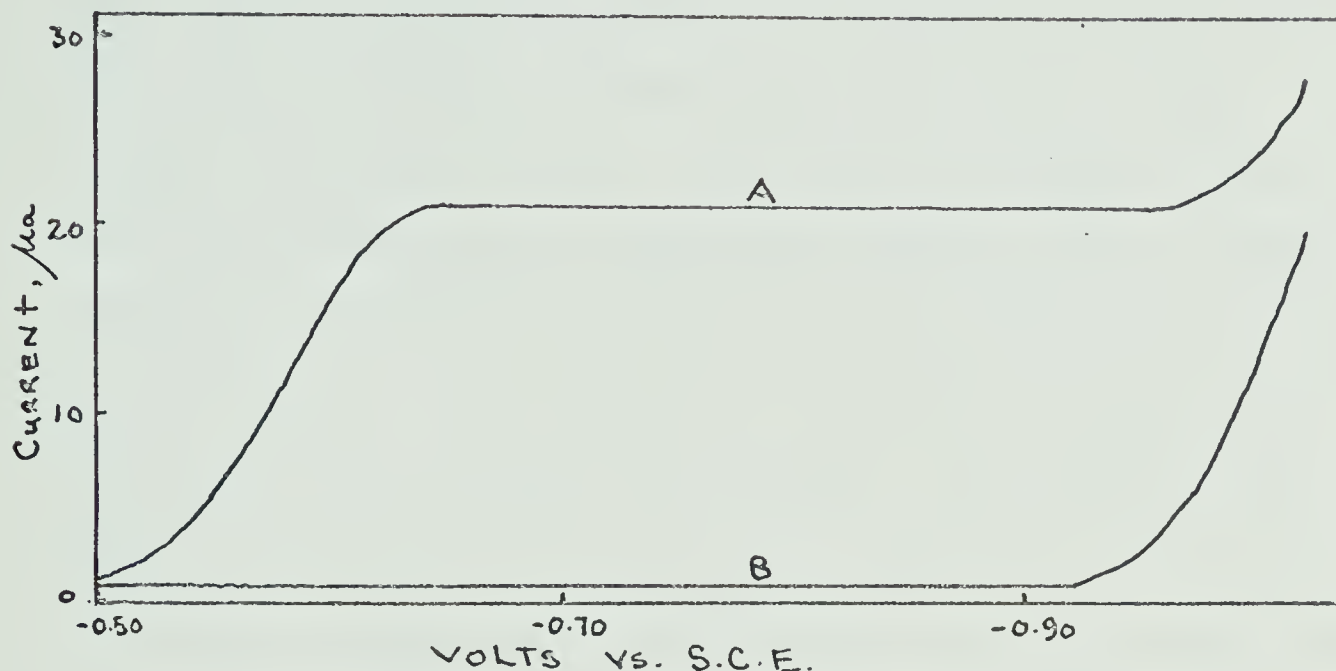
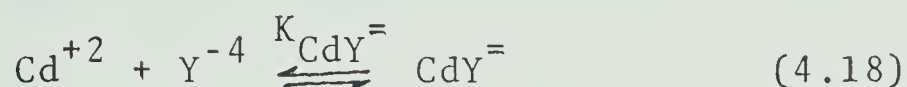
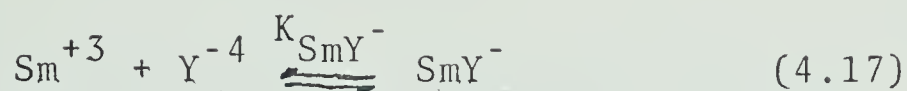


Figure 4.08 A, Current voltage curve for $\text{Cd}^{+2} + \text{Hg} + 2e \rightleftharpoons \text{Cd}(\text{Hg})$ in solution of $4 \times 10^{-3} \text{ M Cd}^{+2}$ and $3 \times 10^{-3} \text{ M Zn}^{+2}$; B, current voltage curve for $\text{Zn}^{+2} + \text{Hg} + 2e \rightleftharpoons \text{Zn}(\text{Hg})$ in solution of $3 \times 10^{-3} \text{ M Zn}^{+2}$ solution. pH is 4.2, μ is 0.1, 0.001% gelatine. Temperature is $21.0 \pm 0.2^\circ\text{C}$. The zinc reduction starts at about -1.0 volts vs. S.C.E.

The procedure for the determination of the ratios of the conditional equilibrium constants was to introduce 10 ml aliquots of standard Cd^{+2} solution and Sm^{+3} , Nd^{+3} , Gd^{+3} or Zn^{+2} solution into a 70 ml electrolytic cell. (Figure 4.07). 10 mls of 0.1M acetic acid-acetate buffer of pH 4.2 and 0.001% gelatin were added. The ionic strength was adjusted to 0.1 with potassium nitrate. Water was then added to bring the volume to 50 mls within 0.5 mls.

The solution was then deaerated with nitrogen and after attainment of constant temperature, a diffusion current measurement was made at -0.70 volts versus S.C.E. A small amount of EDTA, enough to react with 25 percent of the cadmium, was added; more nitrogen was bubbled through and after allowing a minute for convection to cease another diffusion current measurement was made. More EDTA was added and the procedure repeated until further addition of EDTA did not decrease the diffusion current significantly. The diffusion current measurements were corrected for dilution if necessary. The ratio of the conditional equilibrium constants was then calculated in the manner suggested by Schwarzenbach and described previously (Chapter II, Section 2.0 3).

Additional determinations were made for different initial amounts of Cd^{+2} and Sm^{+3} , Gd^{+3} , Nd^{+3} or Zn^{+2} to observe if there was any effect on the ratio of conditional equilibrium constants caused by changing the ratio of cadmium concentration to metal ion concentration. No evidence for this effect was found. However, the effect of change of concentration ratio was considered in a theoretical manner by Ringbom (53). Applying his treatment to the calculation of the ratio of an unusual or modified form of the conditional equilibrium constants, consider the main reactions of samarium and cadmium with EDTA.



K_{SmY^-} will be larger than K_{CdY^-} . As has been discussed and shown previously, the larger the difference between the constants, the more accurately can Sm^{+3} be determined by titration. The method of calculating the influence of Cd^{+2} on the determination of Sm^{+3} is to consider the reaction between Cd^{+2} and EDTA as a side reaction. If this is the only side reaction; α_4 , the fraction of free EDTA present as the tetravalent anion would be given as

$$1/\alpha_4 = 1 + [\text{Cd}^{+2}] K_{\text{CdY}^-} \quad (4.19)$$

The conditional equilibrium constant for SmY^- (K'_{SmY^-}), is then given as

$$K'_{\text{SmY}^-} = \frac{C_{\text{SmY}^-}}{C_{\text{Sm}^{+3}} C_{\text{Y}^{-4}}} = \frac{[\text{SmY}^-] \cdot \alpha_4}{[\text{Sm}^{+3}] [\text{Y}^{-4}]} \quad (4.20)$$

Therefore,

$$K'_{\text{SmY}^-} = K_{\text{SmY}^-} \cdot \alpha_4 = \frac{K_{\text{SmY}^-}}{1 + [\text{Cd}^{+2}] K_{\text{CdY}^-}} \quad (4.21)$$

Of course, if Sm^{+3} , Y^{-4} or SmY^- are involved in other side reactions, as is likely, additional coefficients must be considered.

Equation 4.21 can also be written as

$$\log K'_{\text{SmY}^-} = \Delta K + p\text{Cd}^{+2} \quad (4.22)$$

Using the same considerations, the following equation can also be derived

$$\log K'_{\text{CdY}^{\pm}} = \Delta K + p\text{Sm}^{+3}. \quad (4.23)$$

Equations 4.22 and 4.23 indicate that $K'_{\text{SmY}^-}/K'_{\text{CdY}^{\pm}}$ will be related to the ratio of metal ion and indicator ion concentrations.

It should be pointed out that the side reaction of Y^{-4} with H^+ ions is important. Equation 4.19 can then be written as

$$\begin{aligned} 1/\alpha_4' &= 1 + [\text{H}^+] \cdot K_{\text{HY}^{\pm}} + [\text{H}^+]^2 K_{\text{H}_2\text{Y}^=} + [\text{H}^+]^3 \cdot K_{\text{H}_3\text{Y}^-} \\ &\quad + [\text{H}^+]^4 \cdot K_{\text{H}_4\text{Y}} + [\text{Cd}^{+2}] K_{\text{CdY}^=} \\ &= 1/\alpha_Y^{-4} + 1/\alpha_4 \end{aligned} \quad (4.24)$$

Equation 4.24 indicates that a metal ion such as Cd^{+2} will interfere in the titration of another ion such as Sm^{+3} only in the pH range where $\alpha_4 > \alpha_Y^{-4}$.

Ringbom made the general statement, "When a metal, M_I is titrated complexometrically in the presence of a second metal M_{II} , the logarithmic conditional stability constant, $\log K'_{\text{M}_\text{I}\text{T}}$ equals the difference between the logarithmic stability constants of the two complexes increased by $P_{\text{M}_{\text{II}}}$."

TABLE 4.02 DETERMINATION OF THE RATIO OF THE CONDITIONAL
EQUILIBRIUM CONSTANTS ($K'_{\text{GdY}^-}/K'_{\text{CdY}^{=}}$) FOR GADOLINIUM NITRATE
AND CADMIUM NITRATE SOLUTIONS

μ is 0.1; T is $21.0^\circ \pm 0.02^\circ\text{C}$; p_{aH} is 4.2; 0.001% gelatine is present. The initial amounts of Cd^{+2} and Gd^{+2} present are 1.971×10^{-4} and 1.720×10^{-4} moles respectively.

EDTA $\times 10^4$ moles added	Moles at equilibrium $\times 10^4$				log $(K'_{\text{GdY}^-}/K'_{\text{CdY}^{=}})^*$
	$C_{\text{Cd}^{+2}}$	$C_{\text{CdY}^{=}}$	C_{GdY^-}	$C_{\text{Gd}^{+3}}$	
0.498	1.837	0.134	0.355	1.365	0.55 ± 0.04
1.023	1.620	0.351	0.672	1.048	0.47 ± 0.04
1.519	1.431	0.540	0.979	0.741	0.54 ± 0.02
2.018	1.203	0.768	1.250	0.470	0.62 ± 0.05
2.533	0.869	1.102	1.431	0.289	0.59 ± 0.03
3.047	0.499	1.472	1.575	0.145	0.57 ± 0.04
					AV = 0.55 ± 0.06

* Averages of Three Determinations.

Table 4.02 shows the results of the determination of the ratio of K'_{GdY^-} to K'_{CdY^+} for 1.97×10^{-4} moles of Cd^{+2} and 1.72×10^{-4} moles of Gd^{+3} . The results indicate the absence of an appreciable amount of kinetic current for cadmium because the ratio of conditional equilibrium constants is essentially constant, i.e., independent of the amount of EDTA added. The current reading observed after the addition of EDTA is dependent, in the absence of kinetic current, on the ratio of the conditional equilibrium constants. It should be proportional to the concentration of Cd^{+2} present. In the presence of kinetic current the expected current reading will be increased by that amount and thus suggests the presence of too much Cd^{+2} . The calculated value of the ratio of conditional equilibrium constants will therefore be larger than it actually is. As more EDTA is added, the kinetic current will be even larger and hence the calculated ratio of conditional equilibrium constants will be even larger. An increase in the ratio of the conditional equilibrium constants as more and more EDTA is added would indicate the presence of kinetic current. The ratio is constant and can therefore be measured by adding any amount of EDTA.

The optimum amount of EDTA to add would be an amount to react with about 25% to 50% of the Cd^{+2} present. This would correspond, in most cases, to the region where the best precision can be obtained as Figure 2.04 illustrates.

TABLE 4.03 DETERMINATION OF ($K'_{MY^{+n-4}}/K'_{CdY^=}$) WHERE
 MY^{+n-4} IS GdY^- , NdY^- , SmY^- AND $ZnY^=$, FOR VARIOUS
 RATIOS OF $C_{Cd^{+2}}/C_{M^{+n}}$.

μ is 0.1, T is $21.0 \pm 0.2^\circ C$, $p_a H$ in all cases is
 4.2.

M^{+n}	Moles Initially Present		$\log K'_{MY^{+n-4}}/K'_{CdY^=}$
	$C_{Cd^{+2}} \times 10^4$	$C_{M^{+n}} \times 10^4$	
Gd^{+3}	1.971	1.720	0.55 ± 0.06
Gd^{+3}	1.971	0.860	0.56 ± 0.07
Gd^{+3}	1.971	0.516	0.59 ± 0.06
Gd^{+3}	0.986	1.720	0.55 ± 0.11
Gd^{+3}	0.986	0.860	0.57 ± 0.05
Gd^{+3}	0.986	0.516	0.62 ± 0.13
Nd^{+3}	1.971	1.693	0.21 ± 0.05
Nd^{+3}	1.971	0.847	0.12 ± 0.08
Nd^{+3}	1.971	0.508	0.19 ± 0.05
Nd^{+3}	0.986	1.693	0.13 ± 0.09
Nd^{+3}	0.986	0.847	0.14 ± 0.06
Nd^{+3}	0.986	0.490	0.09 ± 0.08
Sm^{+3}	2.172	1.709	0.66 ± 0.06
Sm^{+3}	1.971	0.841	0.50 ± 0.11
Sm^{+3}	0.986	0.841	0.58 ± 0.10
Sm^{+3}	1.971	0.504	0.44 ± 0.04
Zn^{+2}	2.106	1.694	0.26 ± 0.04
Zn^{+2}	1.971	0.883	0.19 ± 0.06
Zn^{+2}	0.986	1.765	0.27 ± 0.06

Table 4.03 shows the results of the determinations of the ratios of conditional equilibrium constants for various amounts of cadmium and gadolinium. Also included in the table are similar results for neodymium, samarium and zinc. The values of the ratios of conditional equilibrium constants shown in column four are the average values obtained from the addition of different amounts of EDTA.

Schwarzenbach (31) determined ratios of conditional equilibrium constants, at μ equal to 0.1, of

$$K'_{\text{SmY}}/K'_{\text{CdY}} = 10^{0.65 \pm 0.03} \quad \text{at } p_{\text{C}}^{\text{H}} \text{ of } 4.0$$

$$K'_{\text{NdY}}/K'_{\text{CdY}} = 10^{0.12 \pm 0.03} \quad \text{at } p_{\text{C}}^{\text{H}} \text{ of } 4.2$$

$$K'_{\text{GdY}}/K'_{\text{CdY}} = 10^{0.90 \pm 0.02} \quad \text{at } p_{\text{C}}^{\text{H}} \text{ of } 4.4$$

$$K'_{\text{ZnY}}/K'_{\text{CdY}} = 10^{0.04 \pm 0.04} \quad \text{at } p_{\text{C}}^{\text{H}} \text{ of } 4.2.$$

The present experimental results (TABLE 4.03) were all obtained at a pH of 4.2 and an ionic strength, μ , of 0.1. Table 4.03 shows that the results agree closely with Schwarzenbach's in two of the four systems investigated, namely the $\text{Sm}^{+3}\text{-Cd}^{+2}$ and $\text{Nd}^{+3}\text{-Cd}^{+2}$ systems. The average values of the four are $10^{0.14}$, $10^{0.59}$, $10^{0.58}$ and $10^{0.25}$ for $\text{Nd}^{+3}\text{-Cd}^{+2}$, $\text{Gd}^{+3}\text{-Cd}^{+2}$, $\text{Sm}^{+3}\text{-Cd}^{+2}$ and $\text{Zn}^{+2}\text{-Cd}^{+2}$ respectively. The precision of each is approximately $10^{0.09}$.

Titration Procedure

The apparatus for the titration of samarium, gadolinium, neodymium or zinc with EDTA using cadmium as the indicator ion was identical to that used for the determination of the conditional stability constant ratios. However, the procedure for the titrations was slightly different. An aliquot of standard cadmium solution was introduced into the titration cell, along with an aliquot of metal ion solution to be titrated. 10 mls of 0.1M acetate buffer (pH 4.2) was added by pipet and the ionic strength was adjusted, to have a final value of 0.1, with potassium nitrate. Deionized water was then added to bring the final volume to 50 mls. After deaeration with nitrogen and attainment of constant temperature a current reading was made at -0.70 volts versus S.C.E. Enough EDTA was added to decrease the current about 80 to 90 percent. Nitrogen was again bubbled through the solution for approximately two minutes, for the purpose of oxygen removal and mixing of the reactants. Following this, a current reading was again made. Enough EDTA was then added to provide an excess over the amount needed to complex both the cadmium ion and the metal ion to be determined. Nitrogen was bubbled through the solution again and following this, a third current reading was made. This reading was the residual current and was subtracted from the other two readings. Correction

TABLE 4.04 DATA FROM THE TITRATION OF 1.710×10^{-4} MOLES OF Sm^{+3}
 WITH 1.086×10^{-4} MOLES OF Cd^{+2} .

[EDTA] is 0.1087 M., μ 0.1, p_aH is 4.2, 0.001% gelatine present.
 Current sensitivity is $2\mu\text{a/cm}$. Total initial volume is 50 ± 0.5 mls.

i(cm)	i(cm)-i(RES)	Vol. EDTA Added mls.	i(CORR)	moles EDTA $\times 10^4$ added	moles Cd^{+2} $\times 10^4$		$\%$ Cd^{+2} Reacted	End Pt CORR $\times 10^4$	End Pt CORR $\times 10^4$
					Remaining	Reacted			
23.40	18.95	0	18.95	0	1.086	0	-	-	-
6.10	1.65	2.451	1.73	2.664	0.099	90.9	1.677	1.718	
4.45	0	2.655	0	2.874	0	0	-	-	
(i(RES))									

for dilution was then made on the second reading. For example, the data for one titration and how it was used is shown in Table 4.04. The value in column seven is the percent cadmium reacted, calculated from Equation 2.10, and the value in column nine is the corrected equivalence point calculated from Equation 2.11. The correction factor was obtained from Figure 4.09 for a ratio of conditional equilibrium constants of $10^{0.58 \pm 0.08}$ and a percent Cd^{+2} reacted of $90.9 \pm 2.5\%$. The value of $10^{0.58}$ is obtained from Table 4.03.

Figure 4.09 is an expanded portion of the correction graphs shown in Figure 2.06 and contains correction factors for ratios of conditional equilibrium constants from $10^{1.0}$ to $10^{0.0}$. These curves were calculated with the aid of a computer.

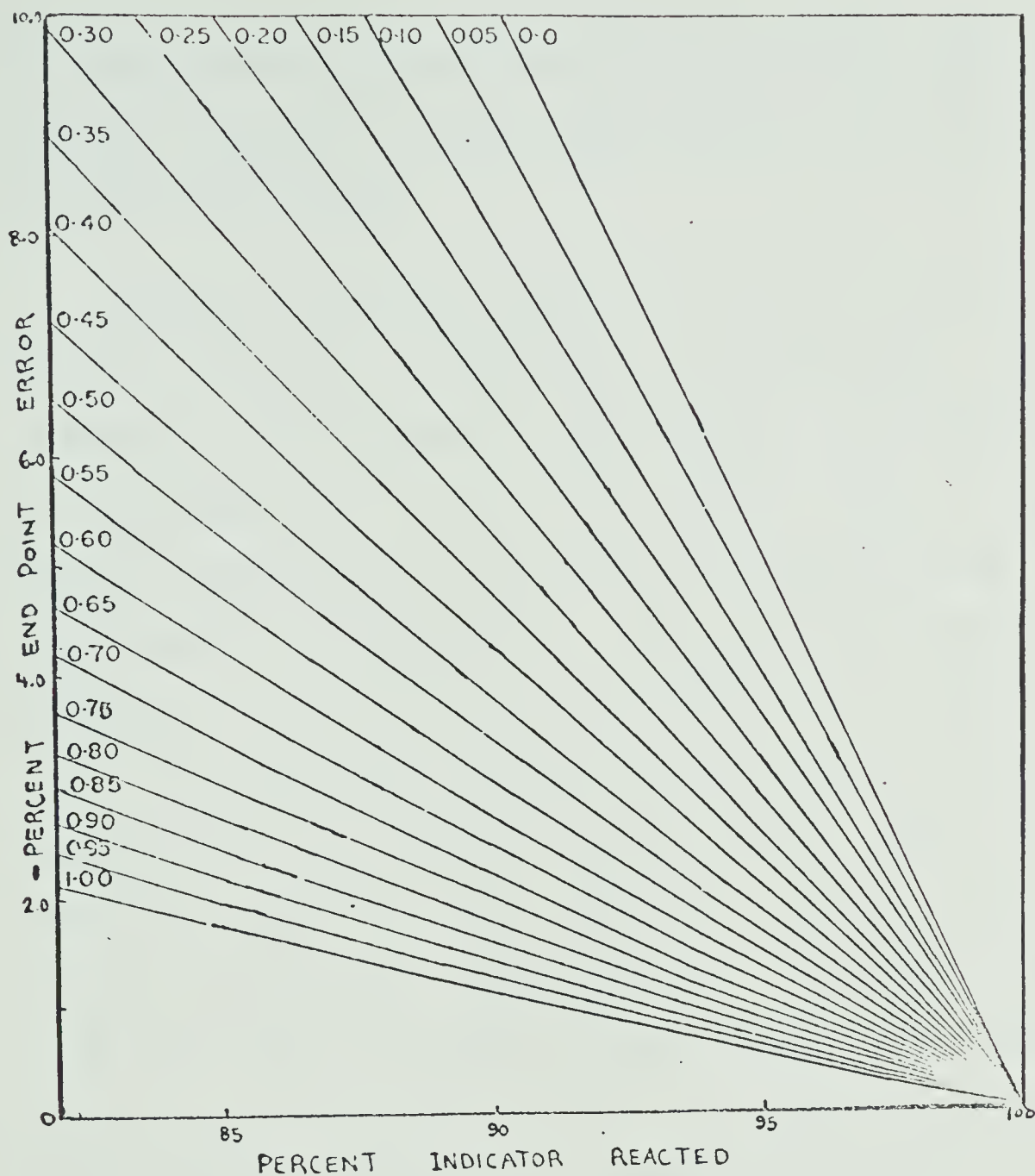


Figure 4.09 Expanded correction graph for the application of the theoretical slope method of end point detection in the range of high percent of indicator ion reacted. Each line corresponds to a different value of $\frac{K'_{MT} + n}{K'_{IndT} + x}$ as noted.

Results obtained from the titration of Sm^{+3} , Gd^{+3} , Nd^{+3} and Zn^{+2} using Cd^{+2} as the amperometric indicator and EDTA as the titrant.

Figure 4.10 shows typical titration curves obtained for the titrations of neodymium and gadolinium. The ordinate is the current in microamperes and the abscissa is the volume of 0.1018 M. EDTA added. Curves A and B are for titrations of gadolinium and curves C and D for the titration of neodymium. The titration curves of neodymium using cadmium as the indicator ion have a ratio of conditional equilibrium constants of about $10^{0.14}$ and therefore are nearly straight lines. They therefore represent one of the most difficult titration curves to use for end point determination. Results of these titrations and titrations of other amounts of samarium, gadolinium, neodymium and zinc are summarized in Table 4.05. All end points were found by the proposed theoretical slope method.

The standard deviation for an individual determination is due to the uncertainty of the values of the percent of Cd^{+2} reacted and the ratio of the conditional equilibrium constants which must be known in order to obtain the correction factor from Figure 4.09. The better the precision of the value of the ratio the better will be the precision of the individual equivalence points found. Similarly the more precise the measurement

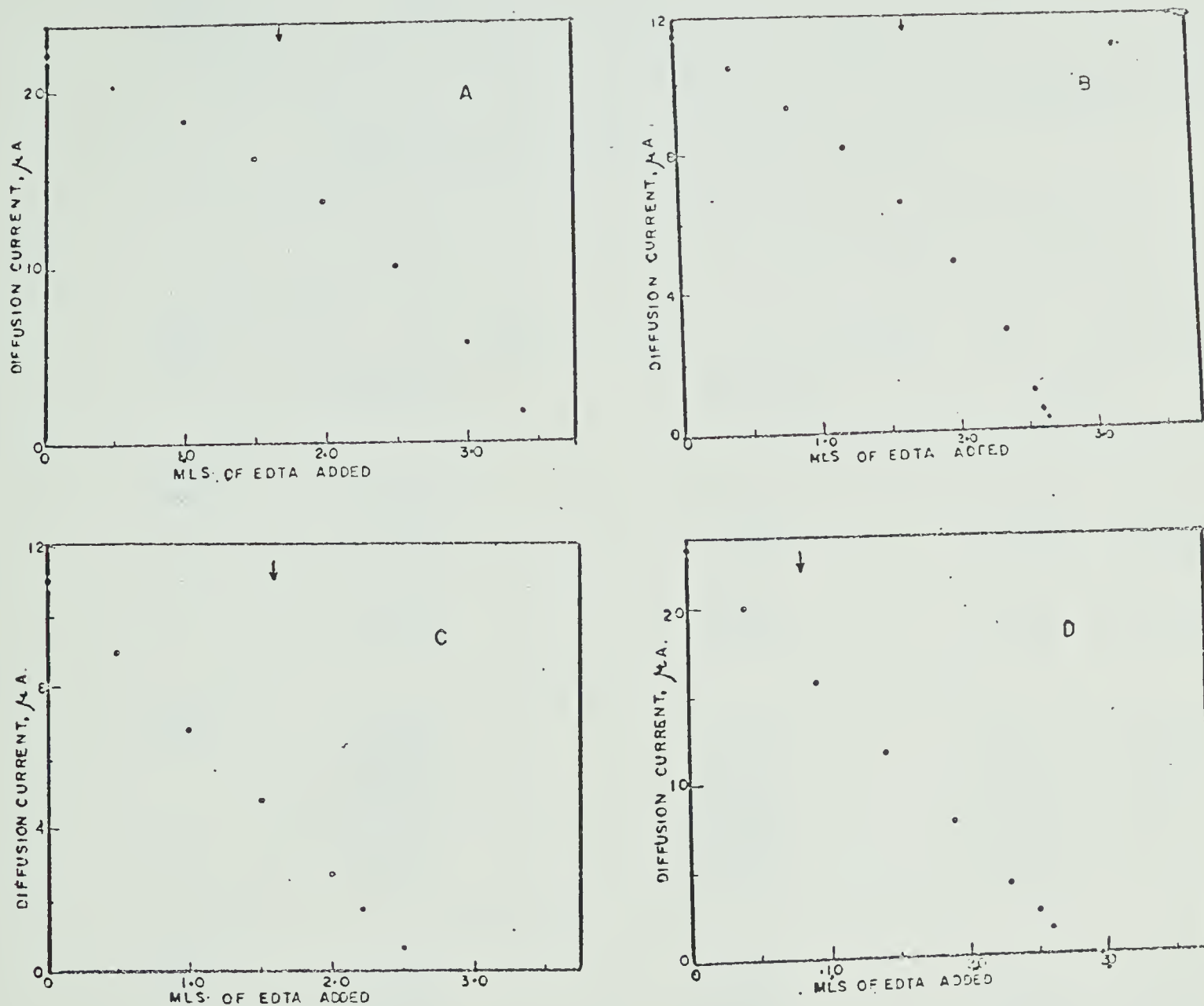


Figure 4.10 Typical titration curves of gadolinium and neodymium. [EDTA] is 0.1018 M. A, titration of 1.670×10^{-4} moles of Gd^{+3} and 1.971×10^{-4} moles of Cd^{+2} in 50 ml. volume; B, titration of 1.670×10^{-4} moles of Gd^{+3} and 0.986×10^{-4} moles of Cd^{+2} in 50 ml. volume; C, titration of 1.693×10^{-4} moles of Nd^{+3} and 0.986×10^{-4} moles of Cd^{+2} in 50 ml. volume; D, titration of 0.847×10^{-4} moles of Nd^{+3} and 1.971×10^{-4} moles of Cd^{+2} in 50 ml. volume. Arrows indicate the equivalence points.

TABLE 4.05 SUMMARY* OF RESULTS OF AMPEROMETRIC TITRATIONS
OF Gd^{+3} , Nd^{+3} , Sm^{+3} AND Zn^{+2} USING Cd^{+2} AS THE AMPEROMETRIC
INDICATOR AND EDTA AS THE TITRANT.

μ is 0.1, p_aH is 4.2, 0.001% gelatine was present.

M^{+n}	$M^{+n} \times 10^4$ moles present	$Cd^{+2} \times 10^4$ moles present	$M^{+n} \times 10^4$ moles found
Nd^{+3}	0.847	1.971	0.836 ± 0.011
	0.847	0.986	0.84 ± 0.02
	0.508	1.971	0.51 ± 0.01
	1.693	0.986	1.70 ± 0.02
Gd^{+3}	1.670	1.971	1.64 ± 0.02
	1.670	0.986	1.64 ± 0.02
	0.835	1.971	0.820 ± 0.02
	0.835	0.986	0.84 ± 0.02
	0.501	1.971	0.52
	0.501	0.986	0.516 ± 0.01
Sm^{+3}	1.709	2.172	1.71 ± 0.030
	1.709	1.086	1.730 ± 0.010
	0.855	2.172	0.860 ± 0.030
	0.513	1.086	0.522 ± 0.010
Zn^{+2}	1.630	2.172	1.69 ± 0.070
	0.845	2.172	0.86 ± 0.04

* See Table A 1.01 in Appendix.

of the concentration of cadmium the more precise will be the end point. The precision is thus a resultant of the errors associated with these two factors.

According to data obtained by Schwarzenbach it appears feasible that the majority of the lanthanide metals can be titrated amperometrically using cadmium as the indicator ion and the T.S.M. as the means of detecting the equivalence points. The choice of conditions such as pH and ionic strength and titrant used may enable more favorable conditional equilibrium constants to be obtained in titration systems where they are initially unacceptable.

Electrochemical interference can be expected from large amounts of metal ions that are more easily reduced than cadmium. These interferences would only reduce the precision of the titration provided that they do not form more stable EDTA complexes than does cadmium or the metal to be determined. In cases where interfering ions form stabler complexes than does cadmium or the metal to be determined, then something must be done such as removing the interfering ion by chemical means.

4.03 - COPPER AS A PHOTOMETRIC INDICATOR FOR THE DETERMINATION OF CALCIUM,

Ramaiah and Vishnu (54) developed a photometric method of estimating calcium by using EDTA as the titrant and $\text{Cu}(\text{NH}_3)_5^{+2}$ as the photometric indicator. It is known that cupric ions in ammoniacal solution form a series of ammonia complexes from $\text{Cu}(\text{NH}_3)^{+2}$ to $\text{Cu}(\text{NH}_3)_5^{+2}$. Bjerrum (55) determined their relative proportions in different concentrations of ammonia. The concentration of the complex $\text{Cu}(\text{NH}_3)_5^{+2}$ increases rapidly as the concentration of ammonia approaches saturation. Ramaiah and Vishnu carried out the titration by measuring the concentration of $\text{Cu}(\text{NH}_3)_5^{+2}$ at 630 m μ . The end points that they obtained were sharp under the experimental conditions of high concentrations of ammonia (>1.5M). They observed, however, that at lower concentrations of ammonia, the end points were not well defined in the sense that the absorbance decreased gradually with addition of EDTA. This increase in curvature in the vicinity of the end point is due to the fact that the ratio of the conditional stability constants ($K'_{\text{CaY}^-}/K'_{\text{CuY}^-}$) decreases as the concentration of ammonia decreases, as described later in this section. For this reason, the system was investigated primarily as a means of easily varying the ratio of conditional constants and illustrating the effectiveness of the T.S.M. and the extrapolation procedure under such conditions.

For this work , a 5.5×10^{-2} M stock solution of calcium nitrate was prepared from Fisher certified reagent calcium nitrate. It was standardized by precipitation as calcium oxalate and weighing, after ignition, as calcium oxide. A 5×10^{-2} M solution of Cu^{+2} was prepared from dissolution of a weighed amount of reagent grade copper wire. A 2×10^{-1} M solution of EDTA was prepared and standardized against magnesium iodate (46).

The procedure for these titrations was identical to that used by Ramaiah and Vishnu. Aliquots of the standard solutions of Ca^{+2} and Cu^{+2} solutions were pipeted into 25 ml. volumetric flasks. The same quantity of ammonia was added to each to bring the solutions to the desired concentration of 2.2 M ammonia. Various amounts of EDTA were added to each flask and the volumes made up to 25 mls with distilled water. Absorption measurements of these solutions were then made on a Beckman D.U. spectrophotometer and the titration curve constructed. Other titrations were carried out in the same manner for ammonia concentrations of 1.1 M and 0.55 M.

Titration at 2.2 M ammonia concentration.

Measurements were carried out at 620 $m\mu$ on solutions containing EDTA, 5.58×10^{-4} moles of Ca^{+2} , 2.430×10^{-4} moles of Cu^{+2} and 2.2 M NH_3 . The titration curve was constructed from these measurements as illustrated in

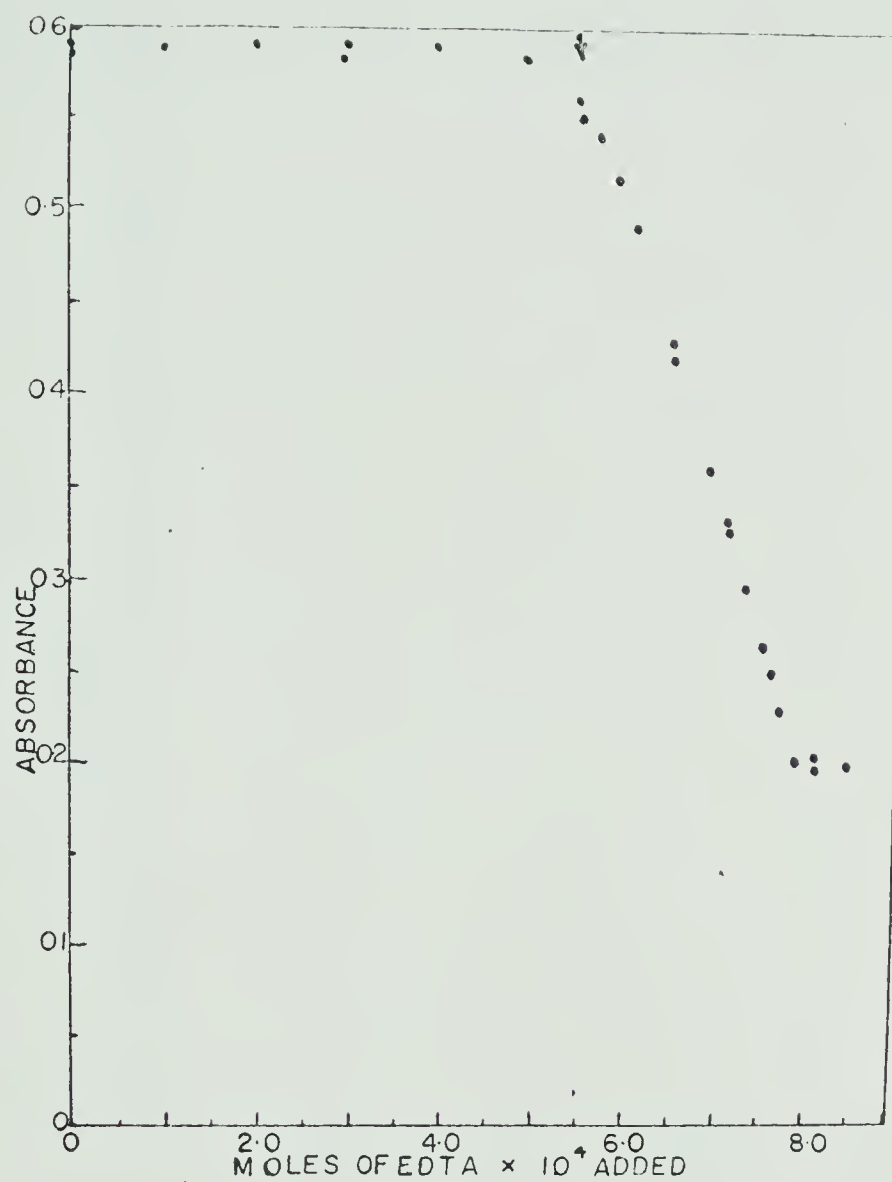


Figure 4.11 Titration of 5.58×10^{-4} moles of Ca^{+2} and 2.43×10^{-4} moles of Cu^{+2} using EDTA as the titrant. $[\text{NH}_3] = 2.2 \text{ M}$. $\lambda = 620 \text{ m}\mu$. Arrow indicates equivalence point.

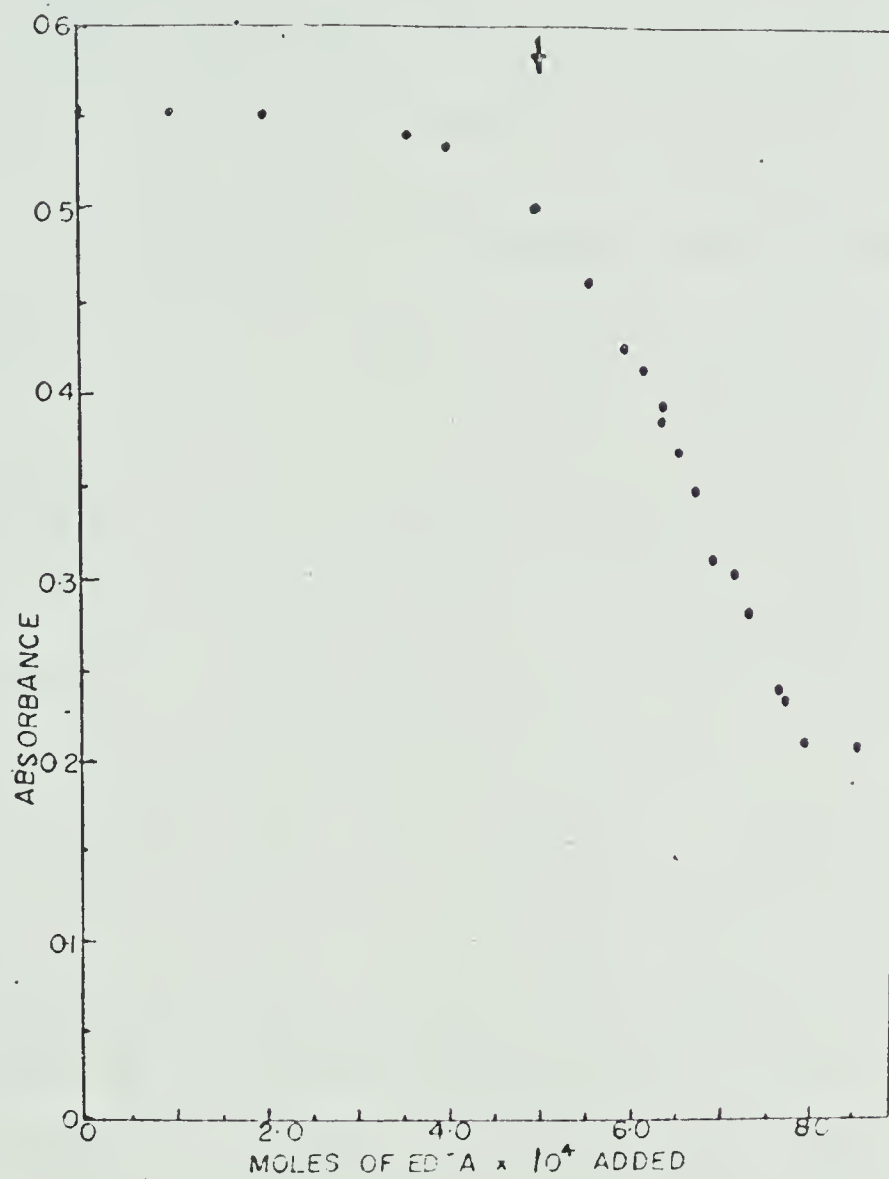


Figure 4.12 Titration of 5.58×10^{-4} moles of Ca^{+2} and 2.43×10^{-4} moles of Cu^{+2} using EDTA as the titrant. $[\text{NH}_3] = 1.1 \text{ M}$. $\lambda = 620 \text{ m}\mu$. Arrow indicates equivalence point.

Figure 4.11. The ratio of $K'_{\text{CaY}}/K'_{\text{CuY}}$ was calculated to be $10^{2.3 \pm 0.4}$ and so the extrapolation procedure was used to determine the end point. A value of $(5.55 \pm 0.05) \times 10^{-4}$ moles of Ca^{+2} was found. The titration curves obtained are similar to those of Ramaiah and Vishnu.

Titration at 1.1 M ammonia concentration.

Investigation of the titration curves resulting from the titration of 5.58×10^{-4} moles of Ca^{+2} , 2.43×10^{-4} moles of Cu^{+2} and 1.1 M NH_4OH (Figure 4.12) permitted the value of $K'_{\text{CaY}}/K'_{\text{CuY}}$ of $10^{1.1 \pm 0.3}$ to be calculated. In a subsequent experiment, 5.58×10^{-4} moles of Ca^{+2} was titrated with EDTA in the presence of a lesser amount of Cu^{+2} (1.46×10^{-4} moles). The concentration of ammonia was 1.1 M. The extrapolation method of end point determination used for this titration is not an acceptable method as an end point of $(4.98 \pm 0.07) \times 10^{-4}$ moles of Ca^{+2} was found. On the other hand, when the theoretical slope method was applied to the same titration correct values are expected and actually a value of $(5.59 \pm 0.07) \times 10^{-4}$ was found.

Titration at 0.55 M ammonia concentration.

Ramaiah and Vishnu observed that at low concentrations of ammonia the end points were not well defined. Investigation of the titration curve (Figure 4.13)

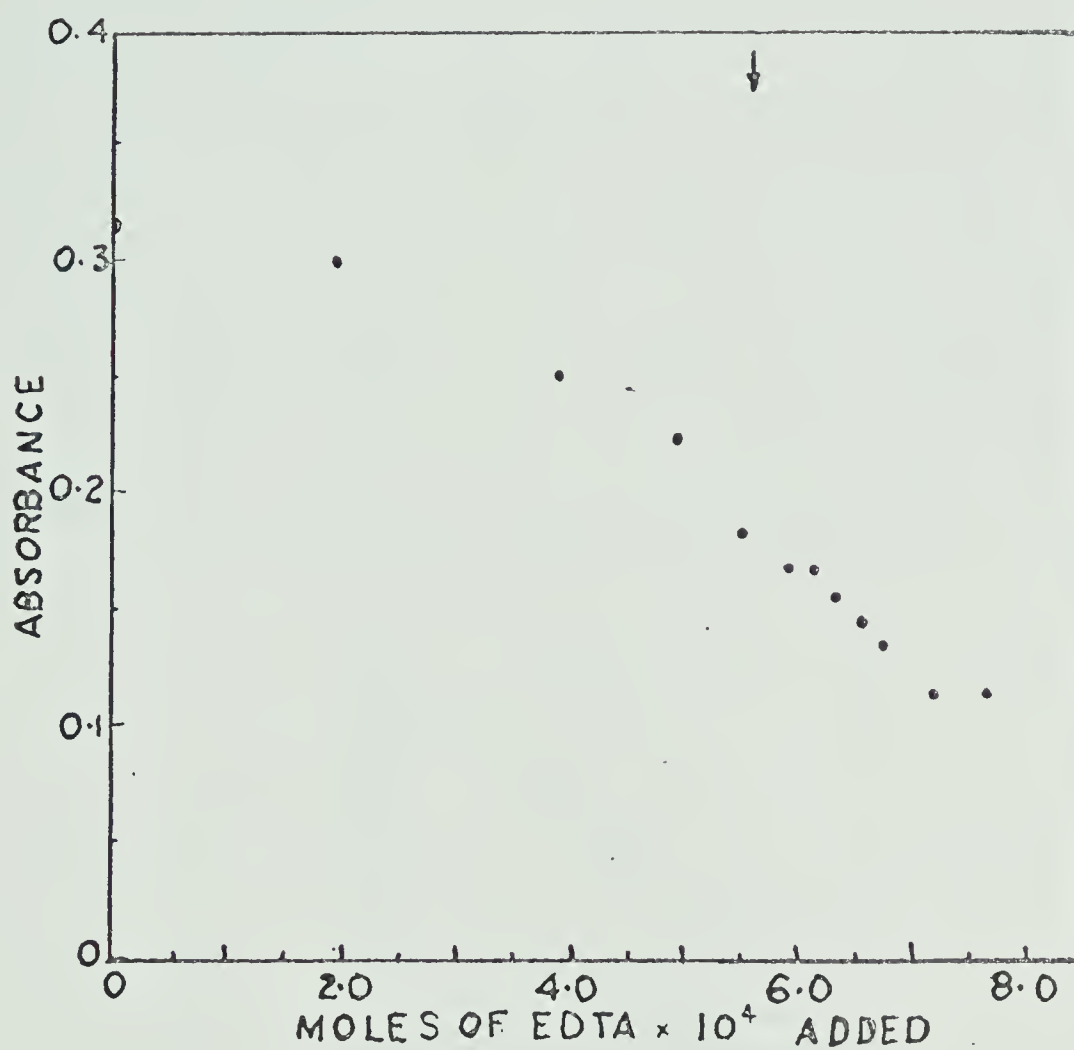


Figure 4.13 Titration of 5.58×10^{-4} moles of Ca^{+2} and 1.46×10^{-4} moles of Cu^{+2} using EDTA as the titrant. $[\text{NH}_3]$ is 0.6 M. λ is 620 m μ . Arrow indicates equivalence point.

resulting from the titration of 5.58×10^{-4} moles of Ca^{+2} and 1.46×10^{-4} moles of Cu^{+2} in 0.55 M NH_3 with EDTA permitted the value of $K'_{\text{CaY}}/K'_{\text{CuY}}$ of $10^{0.49 \pm 0.3}$ to be calculated. When additional titrations were carried out, and the T.S.M. applied, an end point corresponding to $(5.43 \pm 0.07) \times 10^{-4}$ moles of Ca^{+2} was found. The extrapolation method could not be applied because of the large amount of curvature that exists.

A typical titration curve of this type obtained by Ramaiah and Vishnu is shown in Figure 4.14. Using their



Fig. 3. Failure of the spectrophotometric titration of Ca^{+2} with versenate at low concentrations of NH_4OH . λ : 630 m μ . Concentration of Ca^{+2} : 10 mM; concentration of Cu^{+2} : 8 mM; concentration of NH_4OH : 0.53 M; concentration of versenate: 50 mM.

FIGURE 4.14 Titration curve of Ca^{+2} and Cu^{+2} with EDTA (reproduced from Ramaiah and Vishnu (54)).

values and applying the T.S.M. at 94.5% Cu^{+2} reacted gives an end point corresponding to 2.45×10^{-4} moles of Ca^{+2} . They reported that 2.50×10^{-4} moles of Ca^{+2} was initially present. As a conclusion it would be expected that Cu^{+2} could successfully be used as a photometric indicator for the titration of Ca^{+2} in 0.5 M NH_3 .

Effect of Ammonia Concentration on the Ratio of
Conditional Stability Constants ($K'_{\text{CaY}}/K'_{\text{CuY}}$).

The dependence of the experimental ratio of $K'_{\text{CaY}}/K'_{\text{CuY}}$ on the concentration of ammonia is illustrated in Figure 4.15 where the log of $K'_{\text{CaY}}/K'_{\text{CuY}}$ is plotted against $[\text{NH}_3]$. The figure shows that the ratio of the conditional equilibrium constants decreases as the concentration of ammonia decreases. Also included in the

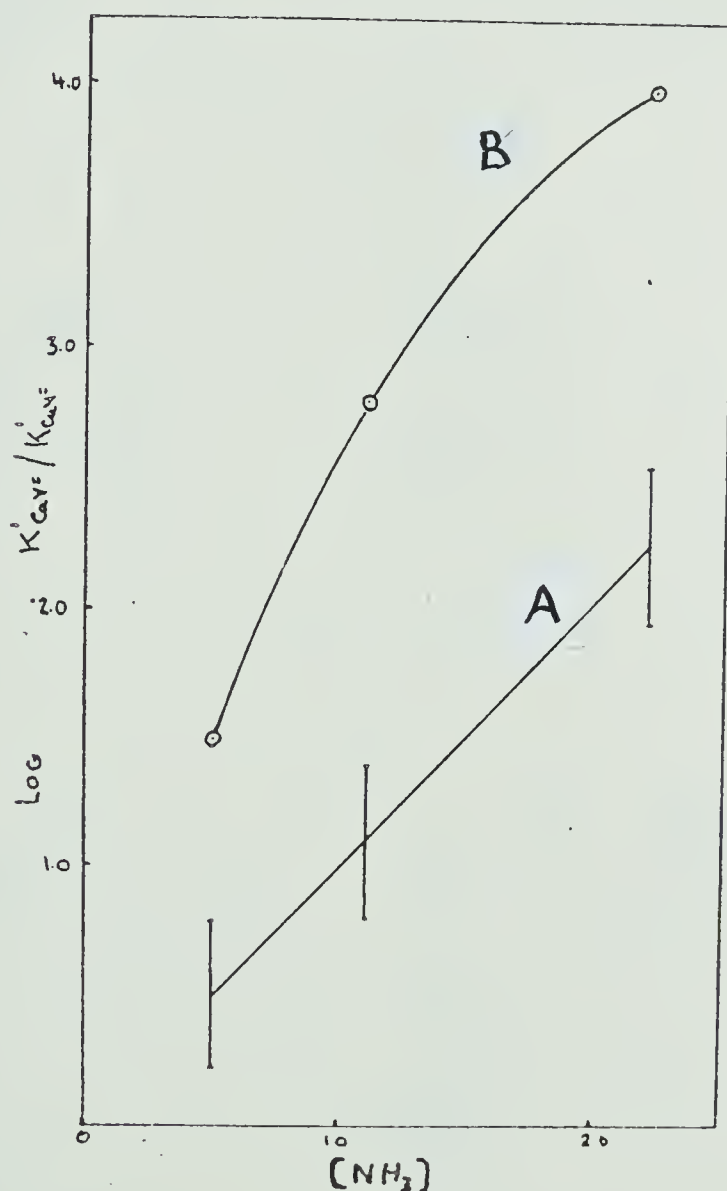
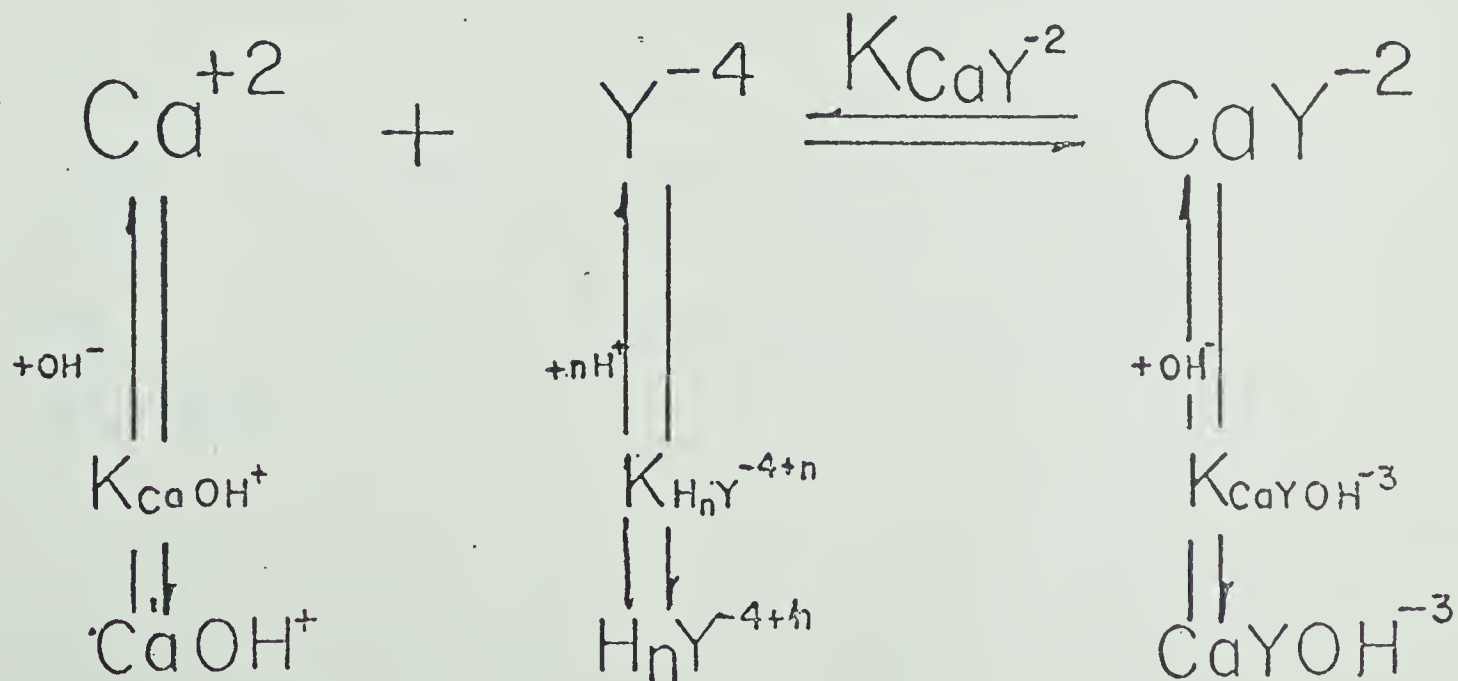
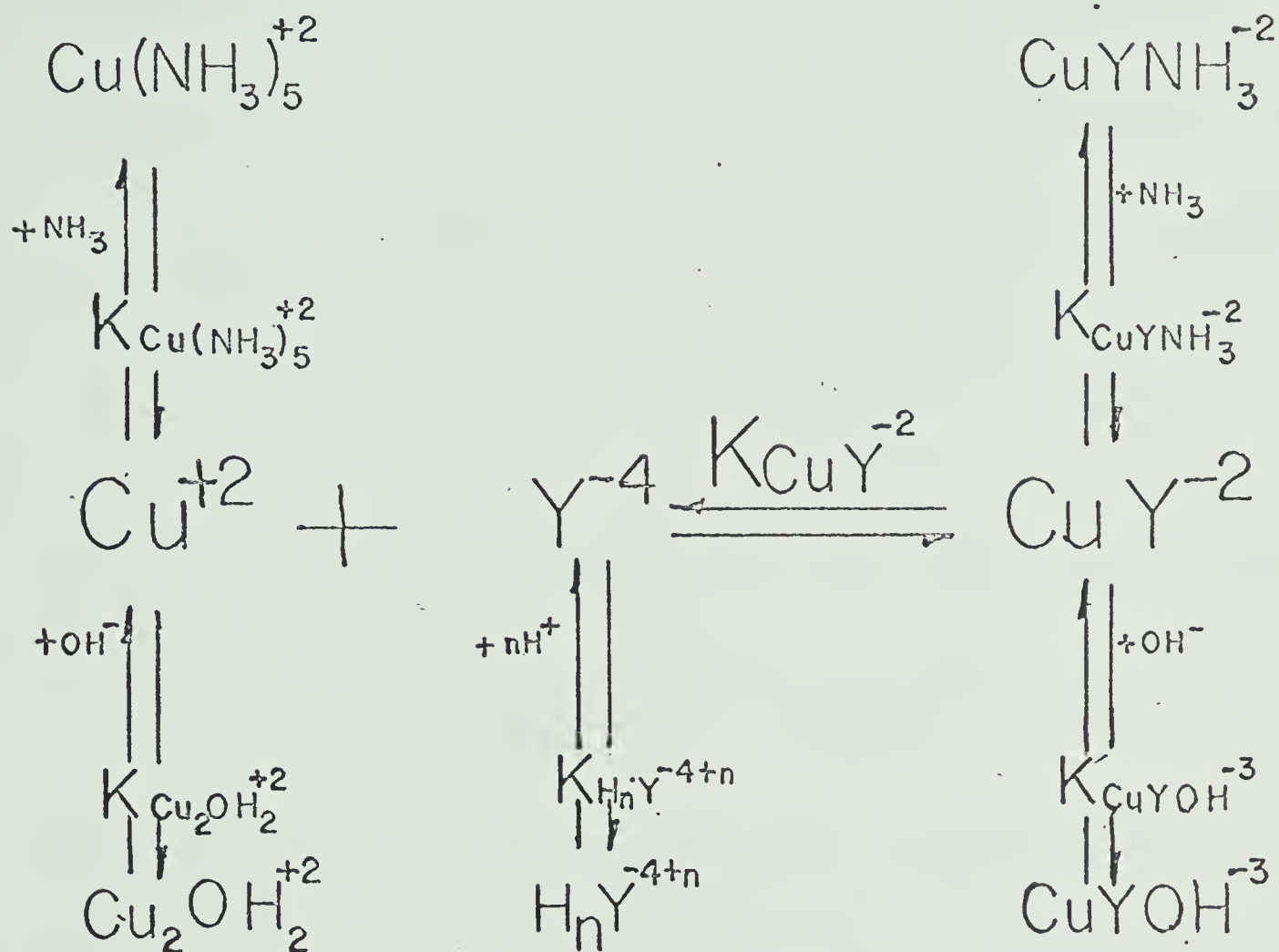


FIGURE 4.15 Dependence of the ratio of K'_{CaY} to K'_{CuY} on the concentrations of ammonia. A, experimental; B, calculated.

figure are theoretical calculations of the ratio at different concentrations of ammonia. These theoretical values were obtained by considering the following equilibria,



The values of the various equilibrium constants are given as (55, 56, 57), $K_{\text{Cu}(\text{NH}_3)_5^{+2}} = 7.4 \times 10^{12}$, $K_{\text{CuY}\text{NH}_3^-} = 10^{2.1}$, $K_{\text{CuYOH}^-} = 10^{2.5}$, $K_{\text{Cu}_2(\text{OH})_2^{+2}} = 10^{17.1}$, $K_{\text{CuY}} = 10^{18.8}$, $K_{\text{CaY}^-} = 10^{10.7}$, $K_{\text{CaOH}^+} = 20$ and $K_{\text{CaYH}^-} = 10^{3.1}$.

The conditional stability constant of CuY^- is written in the form

$$K'_{\text{CuY}^-} = K_{\text{CuY}^-} \frac{\alpha_Y^{-4} \beta_{\text{Ca}^{+2}}}{\beta_{\text{CuY}^-}}$$

and the conditional stability constant of CaY^- is written in the form,

$$K'_{\text{CaY}^-} = K_{\text{CaY}^-} \frac{\alpha_Y^{-4} \beta_{\text{Ca}^{+2}}}{\beta_{\text{CaY}^-}}$$

where α_Y^{-4} is the fraction of free EDTA present as the tetravalent anion, $\beta_{\text{Cu}^{+2}}$ is the fraction of copper ion not complexed with EDTA and is present as the aquated ion; β_{CuY^-} is the fraction of CuY^- that is present as the aquated species, $\beta_{\text{Ca}^{+2}}$ is the fraction of calcium not complexed with EDTA and is present as the aquated ion and β_{CaY^-} is the fraction of CaY^- that is present as the aquated species. Table 4.06 shows the calculated values of these coefficients are 2.2 M, 1.1 M and 0.5 M NH_3 . Also included are the calculated ratio of $K'_{\text{CaY}^-}/K'_{\text{CuY}^-}$.

TABLE 4.06 CALCULATED VALUES OF $\beta_{\text{Cu}^{+2}}$, $\beta_{\text{CuY}^=}$, $\beta_{\text{Ca}^{+2}}$, $\beta_{\text{CaY}^=}$, $\alpha_{\text{Y}^{=4}}$ AND $\log K'_{\text{CaY}^=}/K'_{\text{CuY}^=}$ FOR 2.2 M, 1.1 M AND 0.5 M NH_3 .

$[\text{NH}_4\text{OH}]$	$-\log \beta_{\text{Cu}^{+2}}^*$	$-\log \beta_{\text{CaY}^=}$	$\log \beta_{\text{Ca}^{+2}}$	$\log \beta_{\text{CaY}^=}$	$\log \alpha_{\text{Y}^{=4}}$	$\log K'_{\text{CaY}^=}/K'_{\text{CuY}^=}$
2.2	14.57	2.42	negligible	~0.03	4.0	
1.1	13.08	2.14	negligible	~0.03	2.8	
0.5	11.44	1.82	negligible	~0.03	1.5	

* pOH taken as 12.5 for 2.2 M NH_3 , 12.4 for 1.1 M NH_3 , 12.2 for 0.5 M NH_3 .

Figure 4.15 shows that the theoretical values of the ratio of the conditional equilibrium constants are larger, by a factor of about two, than the experimentally determined values. However, this is undoubtedly due to the uncertainty of the equilibrium constants that are involved in the theoretical calculations. Quoting Reilley (57), "The various equilibria which must be considered in establishing the effective stability constant of a metal chelate are often uncertain by 0.5 log K units".

5. CONCLUSION

Amperometric titrations of metal ions which are not electroactive can be effectively carried out by addition of a second metal ion species which is electroactive. This second metal ion is called an amperometric indicator because it makes it possible to detect an end point. In photometric titrations there are photometric indicators that serve a similar purpose. Such indicators must form less stable complexes with the titrant than does the metal ion to be determined. When the ratio of conditional equilibrium constants of the metal to be determined-titrant and indicator ion-titrant complexes is large (≥ 100) the end point in this type of titration can be found accurately and precisely by the so called extrapolation method. However, when the ratio of conditional equilibrium constants is less than about 100 the extrapolation method becomes less accurate and precise. In such cases a method, called the theoretical slope method, has been proposed as a means of detecting the end point (Sections 2.02, 2.03, 2.04 and 2.05).

To evaluate the theoretical slope method for precision and accuracy it was compared with the extrapolation method. The comparison was carried out statistically using five computer-calculated titration curves having conditional equilibrium constant ratios

of 10 , $10^{1.5}$, 10^2 , 10^3 and 10^4 (Section 3.02). The extrapolation method and the theoretical slope method were both used to detect the end point in each curve. The extrapolation method gives the best precision when the ratio of conditional equilibrium constants is about 10^3 or greater. For lower ratios the precision deteriorates rapidly. A conditional equilibrium constant ratio of at least 100 gives the best accuracy. The accuracy becomes poorer for lower ratios. The theoretical slope method gives better accuracy and precision than the extrapolation method when the ratio approaches one and is recommended as being preferable in such cases. For titrations in which the ratio of conditional equilibrium constants is of the order of 10^3 or greater the extrapolation method gives end points of accuracy comparable to the theoretical slope method and about twice as precise. However, even in such cases the theoretical slope method has the attractive feature of being more rapid.

Also included in the statistical work was an investigation of factors that may influence the precision of end points found by the extrapolation method. Data has been presented which indicates that the extrapolation method is most precise When the angle between the extrapolated lines is as close as possible to 90° and when little extrapolation is required.

The extrapolation method of end point determination

has been illustrated experimentally for the amperometric titration of thorium using copper (II) as the amperometric indicator, EDTA as the titrant and a rotating platinum indicator electrode. A relative precision of 0.8% was obtained when 133 μg of thorium was titrated. The ratio of conditional equilibrium constants ($K'_{\text{ThY}}/K'_{\text{CuY}}=$) for the system was calculated to be $10^{3.4}$.

Amperometric titrations using cadmium (II) as the amperometric indicator and EDTA as the titrant have been also carried out on 5×10^{-5} mole quantities of gadolinium, samarium, neodymium or zinc. The dropping mercury electrode was the indicator electrode. Each of these systems had experimentally determined ratios of conditional equilibrium constants of less than 10. An accuracy and precision of 1 to 3% was obtained when the theoretical slope method was used to detect the end point. The theoretical slope method gave similar precision and accuracy for the photometric titration of calcium in 0.5 M NH_3 , using a copper amine complex as the photometric indicator and EDTA as the titrant.

On the basis of statistical and experimental evidence the theoretical slope method is shown to be a rapid and precise method of end point detection for titration systems where the ratio of conditional equilibrium constants is less than about 100. It can be used as an alternative to the extrapolation method

when the ratios are greater than about 100.

In this thesis, as was pointed out earlier (Section 2.01) not all possible approaches to the problem of end point determination for titration curves employing metal indicator ions have been investigated. In particular, mention of a second end point has been made but not explored. It is suggested that a critical examination of the limitations of the extrapolation method as a means of detecting this end point may give useful results. It can be speculated that the accuracy of the second end point found by the extrapolation method would be a function of the ratio of the conditional equilibrium constants. It has been shown that the first end point found by extrapolation has a tendency to be low if the ratio is low. A second end point found by extrapolation can be expected to be high if the ratio is low. The precision of the second end point found by extrapolation should be affected by angle and extent of extrapolation (ϕ) in the same manner as the first end point. It is suggested that future work may involve investigation of this alternate means of indirectly determining the first end point.

BIBLIOGRAPHY

- (1) J. T. Stock, "Amperometric Titrations", Interscience, N. Y. (1965) p. 100.
- (2) I. M. Kolthoff and J. L. Lingane, "Polarography", Interscience, N. Y. (1952) p. 63.
- (3) J. J. Lingane and I. M. Kolthoff, J. Am. Chem. Soc., 61, 825 (1939).
- (4) Ref. 1, p. 16.
- (5) W. Nernst and E. S. Merrian, Z. Physik. Chem., 53, 235 (1905).
- (6) H. A. Laitinen and I. M. Kolthoff, J. Phys. Chem., 45, 1079 (1941).
- (7) D. J. Ferrett and C. S. G. Phillips, Trans. Faraday Soc., 51, 390 (1955).
- (8) J. Jordan and J. H. Clausen, "Amperometric Titrations", in "Handbook of Analytical Chemistry", Editor in Chief: L. Meites, McGraw-Hill, N. Y. (1963).
- (9) G. Charlot and B. Trémillon, J. Electro Anal. Chem., 3, 1 (1962).
- (10) A. Ringbom and B. Wilkman, Acta Chem. Scand., 3, 22 (1949).
- (11) C. N. Reilley, R. W. Schmid, and F. S. Sadek, J. Chem. Ed., 36, 11, 555 (1959).
- (12) C. N. Reilley and R. W. Schmid, Anal. Chem., 33, 1664 (1961).

- (13) A. Ringbom, "Complexation in Analytical Chemistry", Interscience, N. Y. (1963).
- (14) H. A. Laitinen, "Chemical Analysis", McGraw-Hill (1960) p. 229.
- (15) H. H. Willard, L. L. Merritt, and J. A. Dean, "Instrumental Methods of Analysis", D. Van Nostrand Company, Inc., N. J. (1958) p. 5.
- (16) R. F. Goddu and D. N. Hume, Anal. Chem., 26, 1740 (1954).
- (17) F. Muller, Z. Elektrochem., 40, 46 (1934).
- (18) H. M. Partridge and R. A. Smith, Mikrochemie, 11, 311 (1932).
- (19) A. Ringbom and F. Sundaman, Z. Anal. Chem., 116, 104 (1939).
- (20) P. C. Zamecnik, G. I. Levin, and M. J. Bergman, J. Biol. Chem., 158 (1945).
- (21) D. A. Aiklus, G. Schmuckler, F. S. Sadek, and C. N. Reilley, Anal. Chem., 33, 1664 (1961).
- (22) C. Liteanu and D. Cormos, Talanta, 7, 18 (1960).
- (23) G. Jander and O. Ptundt, Z. Analyt. Chem., 71, 433 (1927).
- (24) V. Majer, Z. Elektrochem., 42, 123 (1936).
- (25) Y. H. Boulard, Bull. Soc. Chim., France, 408 (1936).
- (26) E. Grunwald, Anal. Chem., 28, 1112 (1956).
- (27) J. Mika, Z. Analyt. Chem., 106, 248 (1936).

- (28) V. A. Khadeev, Chem. Abstr., 52, 19670 e. (1958).
- (29) V. A. Khadeev, Chem. Abstr., 54, 6390 i (1960).
- (30) L. A. V. Bazay, Chem. Abstr., 54, 150 d (1960).
- (31) G. Schwarzenbach, R. Gut and G. Anderegg, Helvetica Chimica Acta, 37, 937 (1954).
- (32) D. L. Ball, W. E. Harris and H. W. Habgood, Separation Science, 2(1), 81 (1967).
- (33) Ref. 2, p. 227.
- (34) F. A. Cotton, and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, N. Y. (1962) p. 749.
- (35) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, N. Y. (1962) p. 749.
- (36) H. A. Laitinen, J. Am. Chem. Soc. 71, 1550 (1949).
- (37) R. L. Pecsok, Anal. Chem., 25, 561 (1953).
- (38) H. A. Flaschka, "EDTA Titrations", Pergamon Press, N. Y., (1964) p. 17.
- (39) M. J. Cabell, Analyst, 77, 859 (1952).
- (40) Ref. 13, p. 333.
- (41) W. J. Blaedel and H. V. Malmstadt, Anal. Chem., 23, 471 (1951).
- (42) J. J. Fritz and J. J. Ford, Anal. Chem., 25, 1640 (1953).
- (43) H. V. Malmstadt and E. C. Gotttrabant, Anal. Chem., 26, 442 (1954).
- (44) G. Goldstein, D. L. Manning and H. E. Zittel, Anal. Chem., 34, 358 (1962).

- (45) L. Gordon and C. R. Stine, Anal. Chem., 25, 192 (1953).
- (46) F. Lindstom and B. G. Stephens, Anal. Chem., 34, 993 (1962).
- (47) J. Breckenridge, Ph.D. Thesis, Univ. of Alberta, October, (1966).
- (48) R. Pribil and B. Matyska, Chem. Abst., 46, 2951f, (1952). Reported in ref. 49.
- (49) N. Tanaka, I. T. Oiwa and M. Kodana, Anal. Chem., 28, 1555 (1956).
- (50) R. W. Schmid and C. N. Reilley, J. Am. Chem. Soc., 80, 2101 (1958).
- (51) L. Erdey, "Gravimetric Analysis" Part II, Editor: I. Buzas, Pergamon Press, N. Y. (1965) p. 150.
- (52) Ref. 51, p. 428.
- (53) Ref. 13, p. 124.
- (54) N. A. Bamaiah and Vishnu, Anal. Chim. Acta., 16, 569 (1957).
- (55) Ref. 2, p. 231.
- (56) C. N. Reilley, Anal. Chem. 33, 1664 (1961).
- (57) Ref. 13, p. 294-370.

APPENDIX

TABLE A1.01 RESULTS OF AMPEROMETRIC TITRATIONS OF
 Gd^{+3} , Nd^{+3} , Sm^{+3} AND Zn^{+2} USING Cd^{+2} AS THE AMPEROMETRIC
 INDICATOR AND EDTA AS THE TITRANT.

μ is 0.1, p_aH is 4.2, 0.001% gelatine was present.

M^{+n}	$M^{+n} \times 10^4$ moles present	$Cd^{+2} \times 10^4$ moles present	% Cd^{+2} reacted	Uncorrected End Point	$M^{+n} \times 10^4$ moles found
Nd^{+3}	0.847	1.971	95.4	0.790	0.816
			89.3	0.780	0.844
			93.5	0.800	0.837
			88.6	0.786	0.851
			93.5	0.799	0.836
			97.5	0.819	0.833
			AVERAGE = 0.836×10^{-4} moles, STANDARD DEVIATION = 0.011×10^{-4} , REL. STAND. DEV. = 1.3%.		
Nd^{+3}	0.508	1.971	95.3	0.502	0.519
			89.0	0.474	0.511
			93.6	0.489	0.511
Nd^{+3}	1.693	0.986	87.1	1.580	1.730
			93.4	1.615	1.691
			87.9	1.563	1.699
			94.1	1.604	1.672
			AVERAGE = 1.698×10^{-4} moles, STANDARD DEVIATION = 0.02×10^{-4} , REL. STAND. DEV. = 1.2%.		
Nd^{+3}	0.847	0.986	86.3	0.774	0.850
			94.6	0.786	0.816
			92.2	0.821	0.867
Gd^{+3}	1.670	1.971	92.4	1.621	1.66
			97.6	1.634	1.64
			92.6	1.586	1.62
Gd^{+3}	0.835	1.971	91.7	0.785	0.804
			95.0	0.817	0.83
			94.5	0.788	0.80
			96.2	0.805	0.81
			92.3	0.821	0.84
			AVERAGE = 0.82×10^{-4} moles, STANDARD DEVIATION = 0.02×10^{-4} , REL. STAND. DEV. = 2.4%.		

M ⁺ⁿ	M ⁺ⁿ x 10 ⁴ moles present	Cd ⁺² x 10 ⁴ moles present	%Cd ⁺² reacted	Uncorrected End Point	M ⁺ⁿ x 10 ⁴ moles found
Gd ⁺³	0.501	1.971	92.7	0.506	0.52
			95.3	0.501	0.51
			90.2	0.499	0.52
Gd ⁺³	1.670	0.986	90.0	1.599	1.65
			95.2	1.607	1.63
			98.9	1.615	1.62
			84.7	1.593	1.68
Gd ⁺³	1.670	0.986	86.2	1.58	1.65
			90.8	1.59	1.64
			95.7	1.59	1.61
			98.7	1.61	1.62
			91.0	1.59	1.63
AVERAGE = 1.64 x 10 ⁻⁴ moles, STANDARD DEVIATION = 0.02 x 10 ⁻⁴ , REL. STAND. DEV. = 1.2%.					
Gd ⁺³	0.835	0.986	89.3	0.793	0.82
			97.3	0.803	0.82
			93.9	0.812	0.87
Gd ⁺³	0.501	0.986	87.9	0.510	0.53
			94.3	0.506	0.51
			99.1	0.509	0.51
			90.6	0.497	0.51
			96.6	0.511	0.52
AVERAGE = 0.51 x 10 ⁻⁴ moles, STANDARD DEVIATION = 0.01 x 10 ⁻⁴ , REL. STAND. DEV. = 2%.					
Sm ⁺³	1.709	2.172	88.4	1.71	1.76
			88.7	1.65	1.70
			88.4	1.65	1.70
			99.3	1.65	1.65
			87.6	1.70	1.76
AVERAGE = 1.71 x 10 ⁻⁴ moles, STANDARD DEVIATION = 0.03 x 10 ⁻⁴ , REL. STAND. DEV. = 1.8%.					
Sm ⁺³	1.709	1.086	86.8	1.65	1.71
			90.9	1.68	1.72
			94.5	1.70	1.73
			96.8	1.73	1.75
			90.5	1.69	1.73
			94.2	1.71	1.74
			86.2	1.68	1.74
			90.9	1.68	1.72
			94.8	1.71	1.74
AVERAGE = 1.73 x 10 ⁻⁴ moles, STANDARD DEVIATION = 0.01 x 10 ⁻⁴ , REL. STAND. DEV. = 0.6%.					

TABLE A1.01 (continued).

-141

M^{+n}	$M^{+n} \times 10^4$ moles present	$Cd^{+2} \times 10^4$ moles present	% Cd^{+2} reacted	Uncorrected End Point	$M^{+n} \times 10^4$ moles found
Sm^{+3}	0.855	2.172	91.7	0.821	0.840
			95.2	0.803	0.814
			97.1	0.812	0.818
			99.0	0.826	0.828
			90.2	0.859	0.882
			52.7	0.858	0.875
			94.8	0.861	0.873
			97.4	0.873	0.879
			92.4	0.876	0.894
			95.3	0.865	0.877
			97.6	0.876	0.881
			AVERAGE = 0.860×10^{-4} moles, STANDARD		
			DEVIATION = 0.03×10^{-4} , REL. STAND. DEV. = 3.5%.		
Sm^{+3}	0.513	1.086	83.1	0.500	0.525
			89.1	0.497	0.512
			53.3	0.514	0.523
			97.2	0.522	0.526
			84.0	0.508	0.532
			89.0	0.498	0.513
			93.0	0.505	0.515
			97.3	0.522	0.525
			87.5	0.511	0.529
			92.1	0.510	0.522
			96.2	0.520	0.525
			AVERAGE = 0.522×10^{-4} moles, STANDARD		
			DEVIATION = 0.01×10^{-4} , REL. STAND. DEV. = 1.9%.		
Zn^{+2}	1.69	2.172	96.7	1.58	1.62
			98.8	1.65	1.66
			94.8	1.63	1.68
			98.6	1.66	1.67
			94.8	1.63	1.68
			99.5	1.60	1.60
			79.6	1.53	1.72
			86.9	1.68	1.81
			98.6	1.75	1.76
			80.4	1.50	1.69
			92.1	1.57	1.65
			98.7	1.76	1.78
			91.7	1.59	1.66
			90.0	1.62	1.71
			AVERAGE = 1.69×10^{-4} moles, STANDARD		
			DEVIATION = 0.07×10^{-4} , REL. STAND. DEV. = 4.1%.		
Zn^{+2}	0.845	2.172	82.2	0.737	0.825
			87.4	0.792	0.850
			95.6	0.834	0.854
			89.8	0.875	0.927
			97.2	0.817	0.830
			AVERAGE = 0.857×10^{-4} moles, STANDARD		
			DEVIATION = 0.04×10^{-4} , REL. STAND. DEV. = 4.7%.		

B29886